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THE APPLICATION OF A GELATIN RESIN SYSTEM TO AEROSPACE EXPANDABLE SANDWICH STRUCTURES

PHASE I

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TECHNICAL REPORT AFAPL-TR-65-84

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AIR FORCE AERO PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report was prepared, under Contract No. AF33(615)-2058, by Ivan W. Russell and Nels S. Hanssen of GCA Viron Division, GCA Corporation, Minneapolis, Minnesota. Final reports by three subcontractors, covering four subcontracted efforts, are included as part of this report. The subcontractors are Swift and Company, Chicago, Illinois; Monsanto Research Corporation, Dayton, Ohio; and Archer-Daniels-Midland Company, Minneapolis, Minnesota. The effort was initiated under:

Project Number 8170, "Aerospace Site Support Techniques",
Project Number 3145, "Dynamic Energy Conversion Technology", and
Project Number 7381, "Materials Applications".

In particular it was a development effort in compliance with:

Task Number 817004, "Expandable and Modular Structures for Aerospace",
Task Number 314502, "Solar Dynamic Power Unit", and
Task Number 738101, "Exploratory Design and Prototype Development".

Portions of the study were supported by the Air Force Aero Propulsion Laboratory Directors Discretionary Fund.

The study was administrated under the direction of the Technical Support Division and the Aerospace Power Division of the Air Force Aero Propulsion Laboratory and the Application Division of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The Air Force Project Engineers were Mr. Fred W. Forbes and Mr. Albert Olevitch. This report covers work conducted from June 22, 1964 to May 23, 1965.

The authors wish to thank the Project Monitors, Mr. Fred W. Forbes, Mr. Albert Olevitch, 1/Lt. Anthony Zappanti, and 1/Lt. P. W. Lauderback for their assistance in scheduling the vacuum facilities for experimental work and for their suggestions and thorough acquaintance with the problems of the study. Their efforts have widened the scope of the investigation and have yielded a more useful study.

This report was submitted by the authors August 1965.

ABSTRACT

In the search for optimum materials for use in an expandable sandwich concept of fabricating space structures, a gelatin rigidizing resin system was improved and adapted for use to rigidize space structures. It was demonstrated that a protein system is a desirable system for use with fabric materials. The system provided an easily applied, high strength, space environment resistant material which offers good promise for use in actual space systems.

The final items of the development program were light-weight, self-rigidizing 2-½ ft diameter solar energy concentrators and 3-½ ft diameter by 4-ft high cylindrical space shelter models. These structures were vacuum cured by a plasticizer boil-off process of a gelatin resin system.

This report has been reviewed and is approved:

Peter N. VanSchaik, Chief
Space Technology Branch
Technical Support Division

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SECTION 1

INTRODUCTION

The exploration of space will undoubtedly require large size solar collectors and space shelters. The need for transportation of those items into the space environment makes an expandable structure concept attractive. One concept, which was originated by Mr. F. W. Forbes and Mr. Sidney Allinikov of the Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, is based on the combination of a fabric honeycomb material with a plastic rigidizing resin system. High strength-to-weight ratios are inherent in the sandwich material and complete flexibility and packageability are available with the fabric material. A number of plastic resin systems are available for rigidization of the complete structure.

A feasibility demonstration of this concept using a polyurethane, vapor-cured resin system was conducted under Contract AF33(657)-10409 and is discussed in APL-TDR-64-29. That work was continued under Contract AF33(615)-1243 which furthered the development and produced larger structures based on the expandable honeycomb concept. That work is discussed in AFAPL-TR-64-40, Volume I. Both of these efforts were sponsored by the Air Force Aero Propulsion Laboratory.

The feasibility of utilizing gelatin as a rigidizing media for expandable space structures was also demonstrated by Mr. Forbes and Mr. Allinikov as an Air Force in-house study. Further work by the Air Force Materials Laboratory under Contract AF33(616)-8483 produced some promising structural properties and space applicability information for gelatin. That work is discussed in ASD-TDR-63-444.

This report discusses the outcome of a study which brought together the knowledge gained under the earlier studies of the expandable honeycomb concept and the earlier gelatin development work. This study furthered the development of the expandable honeycomb concept and demonstrated that gelatin is a useful rigidizing media for that application. Portions of this study were supported by the Air Force Aero Propulsion Laboratory Directors Discretionary Fund.

SECTION 2

OBJECTIVES

The ultimate objective of this study was to demonstrate that gelatin could be used as a rigidizing material in combination with a fabric sandwich material to produce expandable space structures and terrestrial shelters. Gelatin formulations, at the time of the study initiation, were available which would rigidize through plasticizer release. It appeared desirable to produce a gelatin formulation which would have improved strength properties, faster cure rates, more resistance to the reabsorption of water, and provide an "on-command" cure mechanism. The higher strength and faster cure requirements were investigated by selecting different plasticizers in a plasticizer boil-off curing system. Resistance to water reabsorption and the "on-command" cure system were approached by a cross-linking mechanism and by investigating the use of collagen, another proteinaceous derivative of gelatin.

1. The space shelter model was a 3-½ ft diameter by 2-½ ft high cylinder with a hemispherical dome top and a flat floor.

2. The solar energy concentrators were 2-½ ft in diameter with 60° rim angles. They used a sandwich-type structural material to provide the required structural rigidity. These concentrators were to be inflated and rigidized in a vacuum environment.

SECTION 3

RESIN SYSTEM RESEARCH

Several areas of development were desired in the resin system research. The first area was one of improvement of the existing gelatin rigidizing resin system to provide a stronger, faster curing, especially adapted resin system for this application, but still based on a plasticizer boil-off curing mechanism. The second area of interest was one of modifying the gelatin resin system such that it could be cured through a vapor catalyst cross-linking mechanism. That resin system would then provide a more water resistant system for use in a terrestrial application.

Three subcontractors were chosen to investigate the modification and improvement of the gelatin system. Swift and Company in Chicago, Illinois, were to devote efforts toward the improvement of the existing resin system. Monsanto Research Corporation in Dayton, Ohio, was selected to work on both the improvement and modification of the gelatin system. Archer-Daniels-Midland Company in Minneapolis, Minnesota, was also chosen to develop a modified system which could be catalyzed and cross-linked.

Reports received from these subcontractors are included in this report with only minor modifications made to the reports as originally submitted. Those reports are included as Appendices to this report.

Swift and Company, in their resin system research study, arrived at a formulation which had sufficiently high solids content but still retained fluidity at room temperature for application to the planned structures. It appeared that all modifications or strong solvents used reduced the final strength of the gelatin films.

Monsanto investigated both improvements and modifications to gelatin. They screened many plasticizers for the improved version and arrived at a satisfactory solution for this application. Attempts to use that formulation at room temperature were unsuccessful. Attempts to modifv gelatin for vapor phase catalyzation greatly reduced the structural strength.

Attempts by Archer-Daniels-Midland to modify gelatin for vapor phase catalysis all resulted in lower strengths.

The research efforts concluded that modifications to gelatin or the addition of strong solvents to gelatin would probably reduce the final strength. An operable resin system was provided for use with space structures.

A plasticizer boil-off resin system was desired which would provide higher strength and more resistance to water absorption. Collagen, a derivative of gelatin which is obtained from the animal hide, appeared to offer better physical properties than gelatin alone. Swift and Company, Chicago, Illinois, was selected to investigate the use of this material for space structure application. A report covering those efforts is also included as an Appendix.

SECTION 4

GELATIN APPLICATION TO SPACE STRUCTURES

A. GENERAL

In order to apply any liquid resin system to the rigidization of space structures, a number of characteristics of that resin system are desirable or necessary. In addition to such things as higher strengths, faster cures, and resistance to the space environment, the resin system must meet the requirements which are imposed by the application technique to be used. Such things as being in a liquid form, being non-toxic, being usable in a regular laboratory environment, and being compatible with other materials used in the overall system are desirable.

The research work conducted by the three subcontractors as discussed in Appendices to this report was used to select a satisfactory gelatin resin system for this application.

B. GELATIN FORMULATION

In developing the gelatin solution for uniformly impregnating and rigidizing structural fabrics, several formulations were prepared as recommended by the sub-contractors. Table 17* lists these formulas. Formulas 2 through 5 were prepared by soaking the gelatin plus humectants (urea or formamide) for 20 minutes in cold water (one half the total amount of water). The balance of the water was then added and the mixture stirred at 140°F for about 30 minutes to obtain complete solution of the gelatin. The solutions were then covered and heated for an additional 16 hours in an oven without stirring. In each case, they became extremely viscous when cooled to 100°F, and acquired a rubbery consistency at room temperature, making them unusable for vacuum impregnation. Formula 5, however, was utilized at an elevated temperature to vacuum impregnate a fiberglass structural fabric. That experiment is discussed in a later section.

The solution from Formula 1, Table 17, was prepared by adding the gelatin with stirring to the water and glycerine heated to 130°F. Complete solubility was obtained in 45 minutes but after cooling to room temperature, that solution also became too viscous for satisfactory vacuum impregnation.

The gelatin solutions prepared from Formulas 6 and 7 were the most promising of all the candidates because of the lower room temperature viscosity and viscosity stability characteristics.

* Tables 1-16 and Figures 1-6 are included in Appendices A, B, and C.

TABLE 17

CANDIDATE GELATIN FORMULATIONS

Formula Number	1	2	3	4	5	6	7	8
				Parts By Weight				
Gelatin	20	17.25	20	20	19	36.25	30.0	25
Water	77.5	69	60	75	74	27.25	38.5	41.25
Urea					4.3			
Polyacrylic Acid					1.9			
Formamide		13.75	20	5				
Clycerine	2.5							
Ethylene Chlorohydrin						18.25	24.5	26.25
Methyl Butynol						18.25	7.0	7.5

TABLE 18

VISCOSITY AT VARYING GELATIN SOLIDS CONTENT

Gelatin Solids %	Viscosity cps 25°C
40	100,000
35	22,000
30	1,480
25	500
22	320

Formula 6, as suggested by Swift and Company, was slightly modified with respect to gelatin-liquefier-solvent ratios and resulted in a solution with more satisfactory working properties. Formulations 7 and 8 were used throughout this contract to impregnate and rigidize the experimental model shelters and collectors as well as the delivered end items. The formulas were selected on the basis of:

a. Ease of preparation,

b. Gelatin solids content,

c. Viscosity,

d. Room temperature viscosity stability,

e. Ease of vacuum impregnation,

f. Reflexibilized laminate stability, and

g. Good strength characteristics.

In the early stages of developing a usable gelatin formulation, 200 gram batches of Formula 7 were prepared by stirring all of the ingredients for three hours in a container heated with steam to 130°F. The volatilized solvents were replaced by adding a solution of water-ethylene chlorohydrin-methyl butynol in the same ratio as shown in the formula. A solution viscosity of about 500 centipoises resulted from that procedure which remained stable for over 30 days. When preparing larger batches of material (2,000 to 12,000 gm) however, a higher viscosity of from 1000-1500 centipoises resulted which was not expected but was not considered unusual as scaling up procedures often result in changes of that type. Dilution of the large batches to 25% gelatin solids gave stable viscosities of from 500 - 700 centipoises.

Later in the program gelatin solution preparation was shortened and standardized to obtain maximum uniformity. The water, ethylene chlorohydrin, and methyl butynol were first mixed together and heated to 100°F. The gelatin was added in increments while rapidly bringing the temperature to 130°F. Stirring was continued for 50 minutes for complete solution. Heating was then discontinued and evaporated solvents replaced by adding a solution of the solvents in the ratio given in Table 17, Formula 8. Table 18 shows the gelatin solids viscosity relationship as determined at room temperature.

The gelatin solutions at 25% and 30% (Formulas 7 & 8) were used to impregnate and rigidize the 2-foot collectors and 3-½ foot shelters during this program.

C. SAMPLE STRUCTURAL MATERIALS

In order to develop techniques for applying gelatin to the full size shelters and collectors, small patches of sandwich type structural material were vacuum impregnated, rigidized, and reflexibilized. These techniques were then applied to 8-inch model collectors, 8-inch model shelters, and finally to the full-size structures.

Ten-inch diameter pillows were fabricated from nylon sandwich, drop thread material and Raypan fiberglass (a truss core configuration material) by sewing the edges of the faces together to permit inflation. Vacuum impregnation with the 30% gelatin formulation at room temperature proceeded satisfactorily. The pillows were rigidized in an 18-inch bell jar equipped with a diffusion pump and a nitrogen cold trap. The uniform fabric saturation resulting from vacuum impregnation plus the good cures obtained demonstrated that this particular gelatin formulation could be utilized to rigidize model collectors and shelters. Table 19 lists the ratios of laminate materials before and after vacuum cure.

TABLE 19

WEIGHT RATIOS OF LAMINATE MATERIALS BEFORE AND AFTER CURE

	Parts by Weight		
	Raypan	Gelatin Solids	Solvents
Before cure	1.02	1	2.3
After cure	1.02	1	0.13

Curing conditions: 8-½ hours to a final pressure of 30 microns

	Parts by Weight		
	Nylon	Gelatin Solids	Solvents
Before cure	.640	1	2.3
After cure	.640	1	0.19

Curing conditions: 10 hours to a final pressure of 2 microns

The nylon and Raypan fiberglass pillows were reflexibilized in an atmosphere of steam. They were then packaged in a sealed Scotch-Pak envelope. No significant change in flexibility had occurred after 45 days. Upon weighing the reflexibilized pillow to determine the new gelatin/solvent ratio, it was noted that the samples had lost some gelatin through drainage; consequently the new ratios were not meaningful. Later experiments used a cross-linking process with formaldehyde which rendered the gelatin non-tacky and rubbery in consistence. That step eliminated the tendency of the gelatin to drain.

One Raypan pillow was vacuum impregnated with a gelatin solution prepared from Formula 5, Table 17 utilizing polyacrylic acid as a cross-linking agent. The solution was heated to 130°F but quickly cooled and gelled upon contacting the fabric. Complete impregnation could only be achieved by heating the structural material. Although the sample became very rigid after vacuum cure, it was felt that impregnating larger structures in that manner would not be practicable for this effort.

D. SHELTERS

1. Eight-Inch Model Shelters

Eight-inch model shelters, fabricated from Raypan 302 fiberglass, were impregnated with the 30% gelatin solution and were vacuum cured with good results. The models inflated fully during the first cure cycle and became very rigid. The models were then reflexibilized in an atmosphere of steam. During that process, some gelatin was lost which resulted in incomplete inflation of the structures during the second cure cycle. The data in Table 20 shows that the gelatin loss was about 50% for the first model. The second model more fully inflated during the second cure cycle and according to the data in Table 21, retained most of its gelatin during reflexibilizing.

It is likely that a lesser amount of gelatin could have been used for Model 2 since the rigidity in both cases seemed equal, although the final cure of Model 1 resulted in a lower gelatin content.

2. Gelatin Impregnation and Cure of Special Structural Fabrics

Several cubes were fabricated to learn the effect of impregnation and rigidization with gelatin on various types of structural materials. One 10 x 10-inch cube consisted of three layers of fiberglass materials. Another cube, 18 x 18 inches, was made with two layers of fiberglass. Both cubes were vacuum impregnated and seemed extremely rigid after vacuum cure.

TABLE 20

WEIGHT RATIOS OF SHELTER MATERIALS

DURING VARIOUS STAGES OF FABRICATION, MODEL 1

	Fabric	Gelatin Solids	Solvents
Before cure	.99	1.0	2.30
After cure	.99	1.0	.03
Average pressure was 20 microns for 16 hours			
After reflexibilizing	2.84	1.0	1.12
After second cure	2.84	1.0	.10
Average pressure was 1 mm Hg for 5 hours			

TABLE 21

WEIGHT RATIOS OF SHELTER MATERIALS

DURING VARIOUS STAGES OF FABRICATION, MODEL 2

Time in Vacuum (hrs)	Fabric	Gelatin Solids	Solvents
0		1.0	2.30
2	1.73	1.0	1.58
4	1.73	1.0	0.85
6	1.73	1.0	0.47
8	1.73	1.0	0.25
10	1.73	1.0	0.16
12	1.73	1.0	0.12
Average pressure was 15 microns			
After reflexibilizing	2.01	1.0	0.66
After second cure	2.01	1.0	0.11

Average pressure was 1 mm Hg for 4 hours

In an effort to reduce total packaging weight, the 10-inch cube was vacuum impregnated with the gelatin solution at 40% solids. The viscosity of that solution was about 100,000 cps at 80°F which permitted brushing the gelatin onto a portion of the cube without drainage from the fabric. The cube was then packaged in a plastic film (provided with an air evacuation valve) with the gelatin solution at the center of several folds of material. After eight hours of vacuum application to the package, the resin had not completely soaked through the fabric. Slightly heating the gelatin with a heat gun resulted in complete impregnation.

This method of gelatin impregnation, while desirable from the standpoint of reduced solvent content, is probably not practicable for larger structures because of the length of time required for complete and uniform saturation.

3. Three and One Half Foot Shelters

a. Experimental

Several methods were employed to reduce the payload weight of a flexible packaged shelter. One method was to reflexibilize a cured structure with steam to a gelatin/solvent ratio just sufficient for flexibility. Another method was to partially remove solvents from a gelatin impregnated shelter in a vacuum chamber.

(1) The first 3-½ ft shelter fabricated from Raypan fiberglass with a nylon liner was vacuum rigidized, reflexibilized, and rerigidized. During the first rigidization, the shelter inflated fully from a folded condition and after 20 hours at 1 mm Hg the structure seemed fully cured (Figure 7). Reflexibilization was accomplished by directing steam to the interior of the shelter which had been covered with a polyethylene film to reduce heat loss (Figure 8). After the structure became flexible, it was folded compactly and packaged in Scotch-Pak. During the second rigidization, complete inflation did not occur possibly due to gelatin drainage. The shelter had been folded, and it appeared that some of the folds were tightly adhered to each other. The weight ratios of the shelter materials during various stages of fabrication are shown in Table 22.

(2) An attempt was made to remove solvents from the second shelter by placing it in a five-foot vacuum chamber while in its plastic impregnation bag and venting the vapors through the tubes used for gelatin impregnation. This procedure proved too slow primarily because of the small diameter of the tubes. A slit made in the plastic bag did not appreciably increase the rate of solvent loss. The bag was then removed and the structure inflated. The cured shelter was not fully inflated and uneven

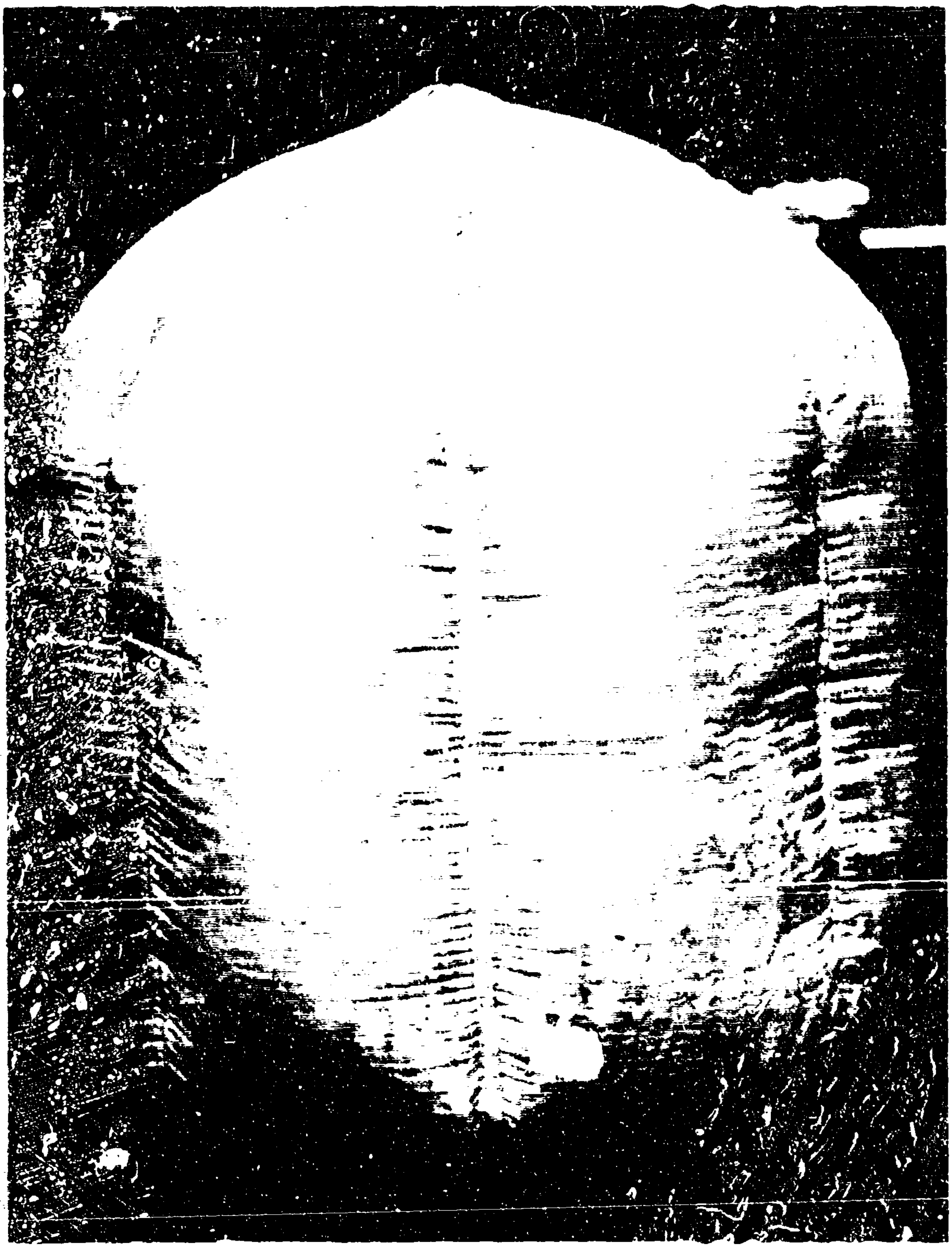

Figure 7 - 3-½ Ft Diameter Shelter Model after First Rigidization

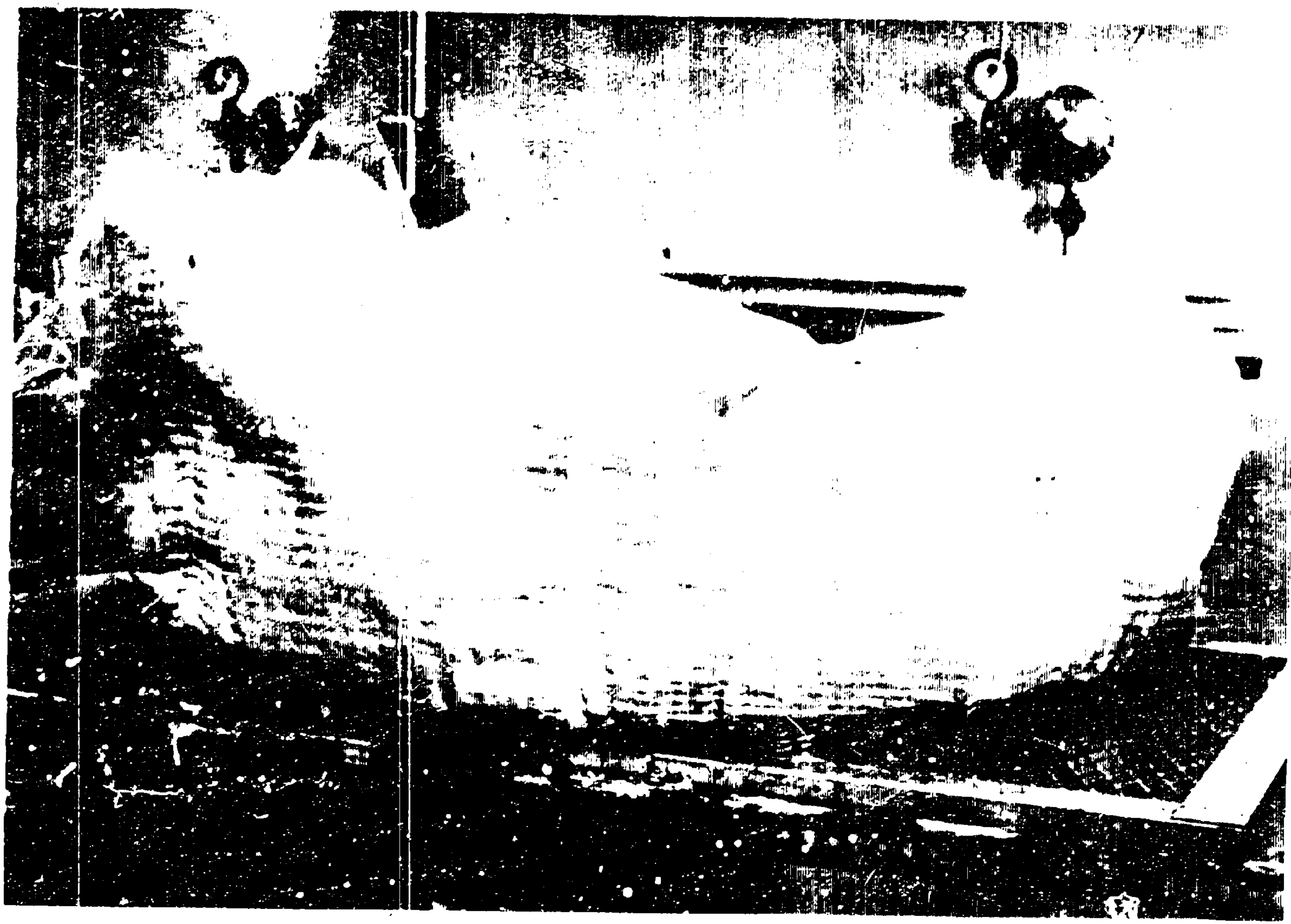

Figure 8 - 3-½ Ft Diameter Shelter Model during Reflexibilization

TABLE 22

WEIGHT RATIOS OF 3-½ FT SHELTER MATERIALS AT VARIOUS STAGES OF FABRICATION,

SHELTER 1

Time	Pressure	Parts by Weight: Fabric	Gelatin Solids	Solvents
First Cure				
0	1 atmosphere	2.14	1	2.80
20 hrs	1 mm Hg	2.14	1	0.13
After Reflexibilizing		2.8	1	1.37
After Second Cure				
7 hrs	3 mm Hg	2.8	1	0.1

resin distribution was noted. Total weights of fabric, gelatin, and solvents before and after cure were as follows:

	Fabric	Gelatin	Solvent
Before cure	5352 g	2480 g	6868 g
After cure	5352 g	2480 g	203 g

b. Shelter End Items

In fulfillment of end item requirements for this effort, two 3-½ ft shelter type structures were vacuum cured at Viron with Air Force personnel in attendance.

(1) On February 23, 1965, a 3-½ ft shelter fabricated from 302 Raypan fiberglass cloth and impregnated with a 30% gelatin solution was vacuum cured (Figure 9). The structure became very rigid after 20 hours in the chamber. Weights and weight ratios of the shelter materials before and after cure are shown in Table 23.

(2) A second shelter was rigidized February 24, 1965, which consisted of a specially designed fabric. The fiberglass structure was a 3-½ ft long cylinder with a 2-½ ft diameter. The cylindrical portion was fabricated into a sandwich construction with an inner face of 181 cloth and an outer face of 1 ply of 181 cloth and 1 ply of 432 cloth. The faces were separated by 1-inch parallel fiberglass webs. The ends of the cylinder were made from Tricon No. H_{51} which is a woven fiberglass cloth with a weight of 37-oz/yd^2, and one layer of a 9-oz/yd^2 fiberglass fabric. These materials were joined together by sewing.

After 24 hours, the structure was very rigid and all of the flutes were fully inflated. Figures 10 and 11 show the cured structure before and after removal from the vacuum chamber and Figure 12 demonstrates the face separation provided by the parallel flutes. Table 24 summarizes the weights and weight ratios of materials before and after vacuum rigidization.

E. SOLAR ENERGY CONCENTRATORS

1. Background Information

a. Structural Materials

The structural materials utilized in this portion of the program were of a special design developed for solar energy concentrator construction under a previous Air Force study. One of the materials

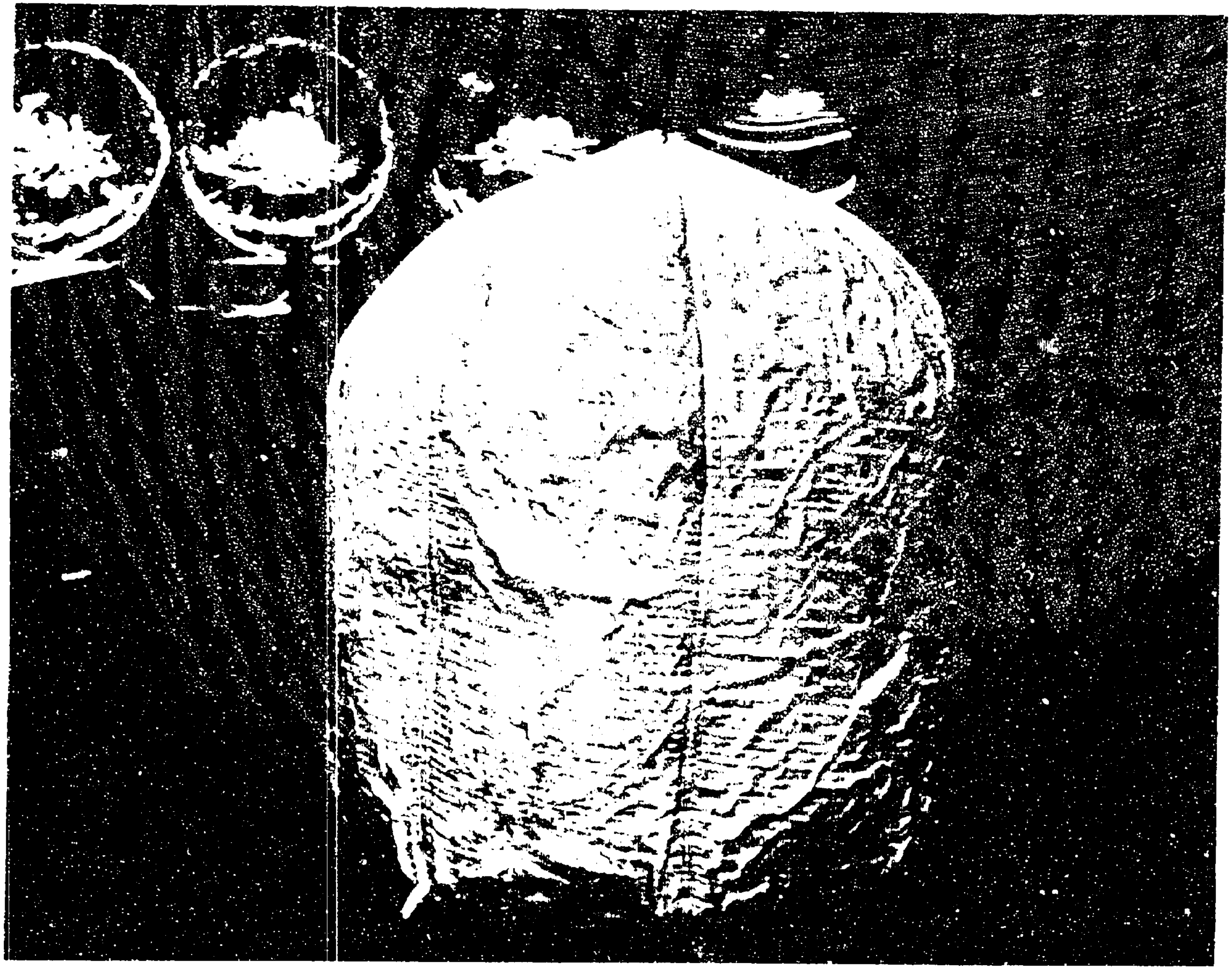

Figure 9 - 3-½ Ft Diameter Shelter Model after Vacuum Cure

TABLE 23

WEIGHTS AND WEIGHT RATIOS OF RAYPAN SHELTER MATERIALS BEFORE AND AFTER CURE, SHELTER END ITEM 1

Before Cure	Fabric	Gelatin	Solvents
Weights	5355 g	2310 g	5380 g
Ratios	2.32	1	2.33
After 20 Hours Vacuum Cure			
Weights	5355 g	2310 g	700 g
Ratios	2.32	1	0.3
Total Final Weight			8365 g

Final Pressure was 200 Microns

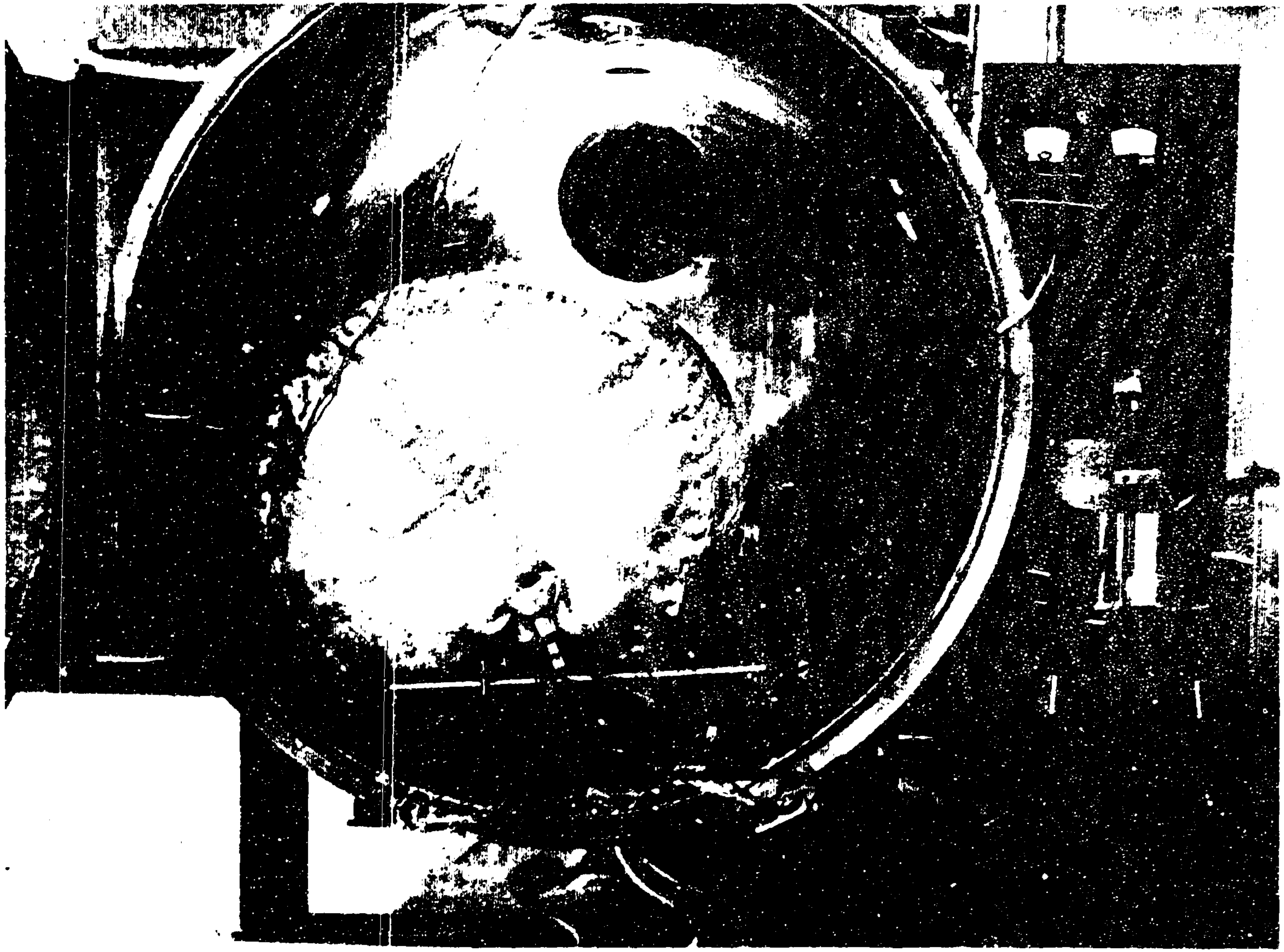

Figure 10 - 2-½ Ft Diameter Cylindrical Space Structure in Vacuum Chamber

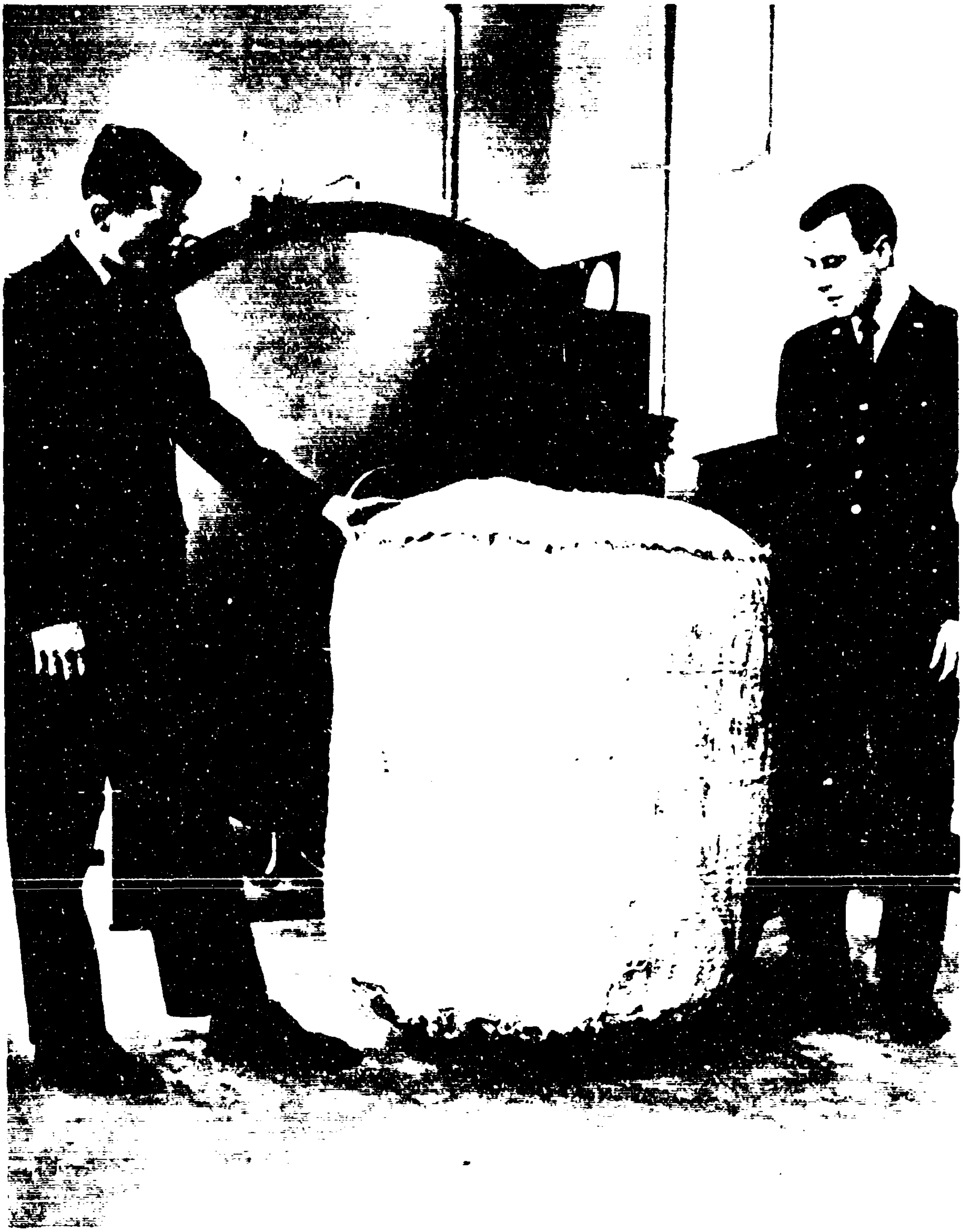

Figure 11 - 2-½ Ft Diameter Cylindrical Space Structure after Vacuum Cure

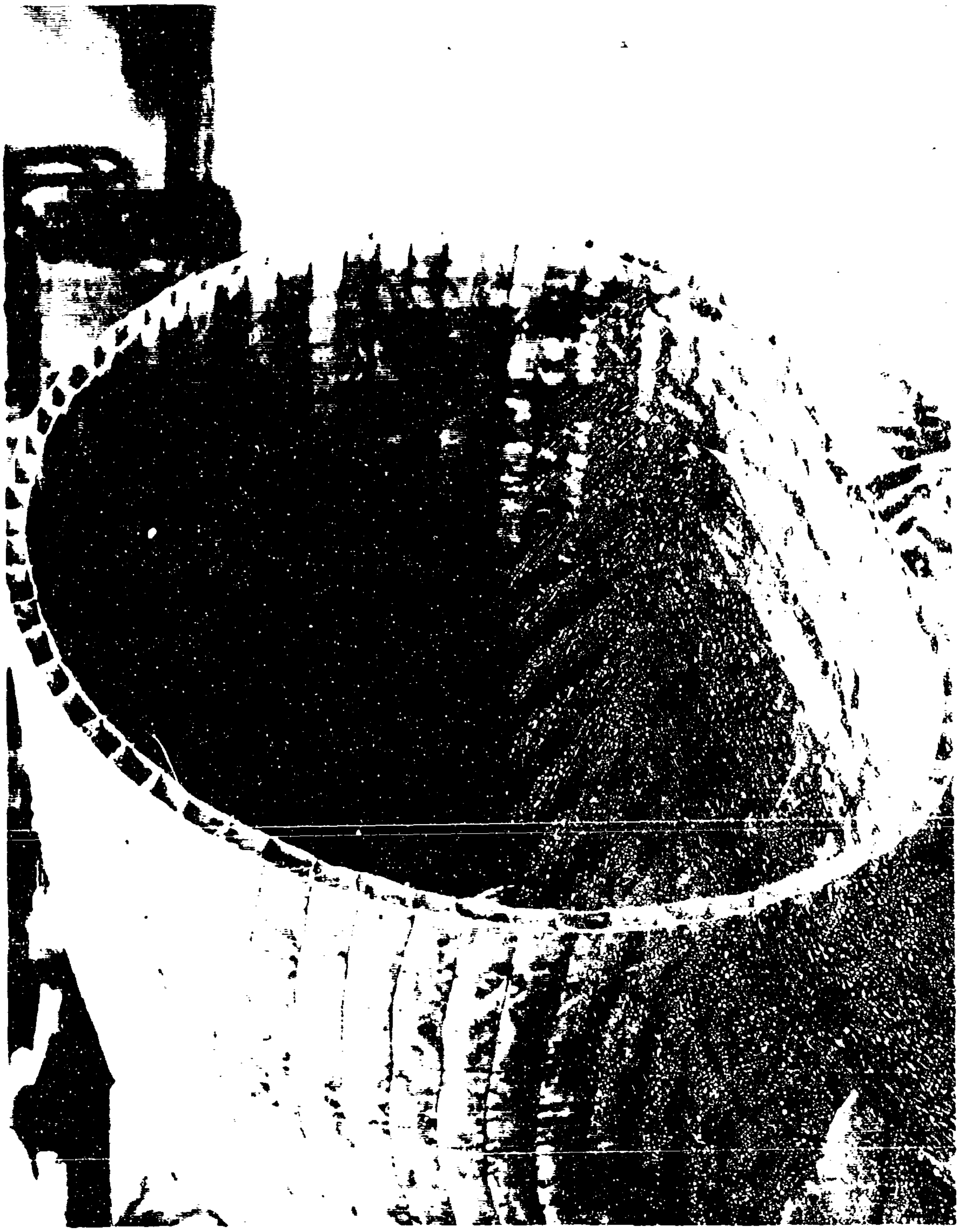

Figure 12 - 2-½ Ft Diameter Cylindrical Space Structure Section

TABLE 24

WEIGHTS AND WEIGHT RATIOS OF CYLINDER TYPE SHELTER BEFORE AND AFTER CURE,

SHELTER END ITEM 2

Before Cure	Fabric	Gelatin	Solvents	Total
Weight, grams	7539	2955	6895	17,389
Ratios	2.55	1	2.3	
After 24 Hours Vacuum Cure				
Weight, grams	7539	2955	896	11,390
Ratios	2.55	1	0.30	

Final pressure was 1 mm Hg

was a three-dimensional fabric woven from nylon with two faces separated by drop threads located in a random (overall) pattern. The other material was similarly woven from dacron. Both sandwich-type fabrics had a face separation of about one inch.

b. Reflective Surface

The reflective surface consisted of a 1 mil (.001 inch) aluminized Mylar tailored with gores to produce a paraboloid with a 60° rim angle.

c. Assembly Fixture

A set of rings was used as an assembly fixture for the two-foot experimental models. The film of assembled Mylar gores was clamped between the rings and inflated by pressurizing between the film and the cover plate. This fixture also mechanically lowered a fabric backing onto the Mylar film and the backing was pressurized to remove wrinkles from the fabric.

d. Flexible Layer

A bonding layer was sprayed or brushed onto the pressurized Mylar. The bonding layer was Epon 872-X-75, a flexible two-component epoxy resin.

e. Gelatin Impregnation

The gelatin solution was uniformly impregnated into the structural material.

2. Eight-Inch Solar Energy Concentrators

Several eight-inch models were constructed early in the program to learn handling techniques and cure conditions of the gelatin solution as applied to the structural materials. Vacuum impregnation of the fabric substrate was satisfactory and good cures were obtained in short periods of time.

Although short cure times were obtained, it was decided that more could be learned by fabricating the full size concentrators on the 28-inch assembly fixture. One reason was that the structural material for the 8-inch models was fashioned from one piece of material and had to be bonded manually. The fabric could not be stretched to remove wrinkles and the difficulty of matching the curved surfaces often resulted in poor bonds.

3. Two-Foot Solar Energy Concentrators

The experimental two-foot solar energy concentrator work is summarized in Table 25.

TABLE 25

GELATIN RIGIDIZED TWO-FOOT SOLAR COLLECTORS

Exp. No.	Bonding Layer	Gelatin/ Fabric	Film Pressure During Assembly	Film Pressure During Cure	Chamber Cure Time	Final Chamber Pressure	Weight Lbs/ Ft^2	Remarks
GN-21	Flexible Epoxy Four 400 g coats sprayed on 50% solids	50/50 nylon	.75 in. Hg	1 in. Hg	17 hrs	400 microns	0.65	Concentric wrinkling. Full cure.
GN-23	Flexible Epoxy Four 400 g coats sprayed on 50% solids	50/50 nylon	1 in. Hg	1¼ in. Hg	7 hrs	350 microns	0.52	Best surface to date. Delivered to WPAFB
GN-25	½ Flexible Epoxy ½ Silicone Rubber Two 400 g coats epoxy and two 400 g coats silicone rubber	40/60 nylon	1 in. Hg	1¼ in. Hg	6.5 hrs	700 microns	0.47	Not cured, air directed through structural material overnight at atmospheric pressure fair surface, good cure.
GN-27	85% normal thickness, Flexible Epoxy. Three 400 g coats sprayed on 50% solids	40/60 nylon	1 in. Hg	1¼ - 1 in. Hg	6 hrs	250 microns	0.48	Partially cured. Air directed through structural material overnight; Concentric wrinkling.

TABLE 25 (Cont'd)

GELATIN RIGIDIZED TWO-FOOT SOLAR COLLECTORS

Exp. No.	Bonding Layer	Gelatin/ Fabric	Film Pressure During Assembly	Film Pressure During Cure	Chamber Cure Time	Final Chamber Pressure	Weight Lbs/ Ft^2	Remarks
GN-28	Flexible Epoxy Four 400 g coats sprayed on 50% solids	50/50 nylon	1 in. Hg	1¼ in. Hg	7 hrs	200 microns	.30	Very good cure, poor surface, much distortion.
GN-29	Flexible Epoxy Four 400 g coats sprayed on 50% solids	40/60 nylon	1 in. Hg	1¼ in. Hg 1¼-1/8 overnight	4 hrs	275 microns	.40	Film pressure dropped overnight. Fabric pattern show through.
GN-32	¼ thicker than usual Flexible Epoxy. Five coats 400 g sprayed on 50% solids	45/55 nylon	1 in. Hg	1-¼ in. Hg	7-½ hrs	500 microns	.47	Not fully cured, directed air between skins about 24 hrs. Surface at first good, but gradually worsened as cure progressed.
GN-37	½ usual thickness Flexible Epoxy Two 500 g coats sprayed on 60% solids	50/50 nylon	1.35 in. Hg	1.35 in. Hg	6-½ hrs one heat lamp directed at backing center	750 microns	.53	Impregnated 15 hrs before curing. Excess resin drained toward outer edge. Center of backing cured after 6-½ hours in chamber. Resin on edge cured in 24 hrs with air at one atmosphere.

TABLE 25 (Cont'd)

GELATIN RIGIDIZED TWO-FOOT SOLAR COLLECTORS

Exp. No.	Bonding Layer	Gelatin/ Fabric	Film Pressure During Assembly	FilmPressure During Cure	Chamber			
GN-38	Flexible Epoxy Four 500 g coats sprayed on 60% solids.	50/50 nylon	1.35 in. Hg	1.35 in. Hg	7 hrs one heat lamp directed at backing center	500 microns	.57	No crease lines. Otherwise same remarks as for GN-37.
GN-40	Flexible Epoxy Four 200 g coats brushed on 100% solids	45/55 Dacron	1.35 in. Hg	1.35 in. Hg	6-½ hrs one heat lamp	500 microns	.86	Impregnated just before cure. Seemed fully cured. Best surface to date. Nearly free of distortion.
GN-42	Flexible Epoxy Four 200 g coats brushed on 100% solids	45/55 nylon	1.35 in. Hg	1.35 in. Hg	6-½ hrs	375 microns	.51	Impregnated just before cure. Good cure. Very good surface. Some fabric show through.
GN-44	Flexible Epoxy ½ usual thickness Two 500 g coats sprayed on 60% solids	45/55 dacron	1.35 in. Hg	1.35 in. Hg	6-½ hrs heat lamp	600 microns	.50	Good surface. No creases. Was fully cured.
GN-46	Tie coats plus Four 500 g coats Flexible Epoxy sprayed on 60% solids	45/55 dacron	1.35 in. Hg	1.35 in. Hg	6-½ hrs heat lamp	550 microns	.65	Best section had tie coat of 46971. Was fully cured.

The flexible layer utilized to bond the structural material to the Mylar and to absorb fabric pattern show through consisted of the following materials:

		Parts by Weight
Part A.	Epon 872-X-75	200.0
	Beetle 216-B	10.1
	MIBK	62.1
	Polysolve	61.2
	Xylol	61.2
	Cab-O-Sil	5.7
		400.3
Part B.	Epon Agent U	13.7

As work progressed, Part A of the above formulation was slightly altered by increasing the amount of epoxy resin to produce a 60% solids content. The purpose was to offset the large amount of resin lost through overspray at the lower solids. Comparative amounts of flexible layer for each concentrator is listed in Table 25.

Collector GN-21, shown in Figure 13, was not fully cured after 2-½ hours, but became very rigid after an additional 15 hours in the 5-foot chamber. During that time, the internal pressure of the collector had dropped which probably caused numerous wrinkles and creases in the reflective surface. The next collector, GN-23, shown in Figure 14, was cured without creases in the reflective surface by maintaining a higher skin stress during assembly and vacuum cure. That collector was sent to Wright-Patterson Air Force Base for evaluation.

Collector GN-25 was made with a modified bonding layer consisting of two degrees of flexibility. The purpose was to provide more flexibility and greater absorption of stresses in that half of the bonding layer adjacent to the structural material. However, no significant improvement was noted. The cured structure seemed sufficiently rigid although a lesser amount of gelatin was used.

A slightly thinner (approximately .020 inch) bonding layer was used in experiments GN-27. In that experiment and in GN-29, the collectors lost inflation pressure during the cure which was probably caused by leaks in the Mylar film. GN-28, was fabricated

Figure 13 - 2-½ Ft Diameter Solar Collector Model Assembled at Low Skin Stress

Figure 14 - 2-½ Ft Diameter Solar Collector Model Assembled at High Skin Stress

utilizing Series 2 nylon with drop threads arranged in parallel rows which is a lighter-weight fabric than the material with random scattered pile. The cured collector weighed 0.30 lb/ft^2, but the reflective surface was very distorted.

GN-32 was made with a slightly thicker (.030 in.) flexible layer but was not completely cured after 7-½ hours. The reflective surface was very good at first but distorted as cure progressed. Air was directed between the fabric skins for about 24 hours to complete cure. The next collector GN-37, was fabricated to learn the effect of reducing the thickness of the flexible layer on fabric pattern show through. Although the thickness was reduced to about .015 in., the fabric pattern seemed about the same as that of GN-38. These two collectors were impregnated about 16 hours before rigidization. It was felt that surface imperfections might be due to uneven gelatin distribution and could be avoided if the gelatin had more time to thoroughly soak into the lower skin of the backing material. That procedure resulted in excessive drainage of the gelatin solution toward the outer edge of the collectors, some of which was redistributed by the vacuum technique. After about seven hours in the vacuum chamber, only the center portions of the collectors had become rigid. Complete cure was accomplished by directing air between the faces of the structural material.

To eliminate the possibility of surface creases or other distortions being caused from entrapped spray solvents, the flexible layers were applied by brush in GN-40 and GN-42. The resulting films were markedly thicker than those applied by spraying. Both collectors were impregnated with the rigidizing resin just before curing which prevented excessive drainage towards the edges. Additional heat lamps were placed in the chamber to provide more moderate temperatures.

GN-40, with a Series 1 dacron backing, was more fully cured after 6-½ hours than GN-42 which employed Series 1 nylon as the backing material. This, at first, seemed unusual as the dacron being heavier than the nylon was impregnated with more gelatin, however, it was felt that the dacron probably had a slightly looser weave which allowed more rapid escape of solvent. Both surfaces were nearly free of distortion shortly after cure, but later changed in appearance similar to collectors made with the flexible layer sprayed on. Figure 15 shows the reflective surface of GN-40 several days after cure.

Collector GN-44 was fabricated with the same bonding layer thickness as GN-37. A temperature of about 90°F was maintained on the backing material with three heat lamps and the gelatin became fully cured after 6-½ hours. The reflective surface was free of wrinkles and creases.

Figure 15 - 2-½ Ft Diameter Solar Collector Model after Vacuum Cure

Another collector was assembled and cured to learn the effect of an improvement in the Mylar - flexible layer bond. The pressurized film was divided into three sections and sprayed with the following adhesives:

Section 1, Dupont 46960

Section 2, Dupont 46971

Section 3, Control

Four coats of the flexible epoxy formulation were sprayed and the dacron backing bonded. After vacuum rigidizing the collector with gelatin; Section 1 had partially delaminated, Section 2 seemed to have less fabric pattern show through than did Section 3, and it appeared that a better bond had resulted from the Dupont adhesive 46971.

4. Delivery of Solar Collector End Items to Wright-Patterson Air Force Base

Four two-foot solar collector composites were prepared at Viron for delivery to Wright-Patterson during the week of 15 March 1965. The schedule was as follows:

Composite	1	2	3	4
Gelatin Impregnated at:	Viron	WPAFB	Viron	WPAFB
Cured at:	Viron	WPAFB	Not cured	WPAFB
Date:	3-12-65	3-17-65		3-16-65

Tables 26, 27, and 28 present a detailed account of materials, procedures, cure conditions, and results of those experiments. Thermo-couples were located in various areas of the structural fabric outer skin. Heat was supplied by infrared lamps controlled with a voltage regulator to keep temperatures moderate and to offset the effects of the cold wall on Composites 2 and 4.

a. Composite 1

RIGIDIZED 12 MARCH 1965 AT VIRON

Procedure and Materials

(1) Sixteen gore, 1 mil aluminized Mylar, acetone washed.
(2) Fabricated at 1.35 in. Hg.
(3) Brushed four 200 gram coats of the following:

	Parts
Epon 872-X-75	100.0
Cab-O-Sil	1.5
PC 1244	.3
Agent U	4.6

(4) Series 1, sample 2, nylon bonded to fourth coat.
(5) Vacuum impregnated with the following:

Gelatin (25%)	400 g.
Water	660
Ethylene Chlorohydrin	420
Methyl Butynol	120
	1600 g.

(6) Rigidization
  (a) 1.25 in. Hg. held on Mylar
  (b) 6-½ hr cure time. Final pressure was 260 microns.
  (c) Infrared heat lamps used to keep temperature of materials moderate.
(7) Remarks: Good Surface. No creases after one week.

Table 26 lists vacuum data for this collector.

b. Composite 2

RIGIDIZED 17 MARCH 1965 AT WRIGHT-PATTERSON AIR FORCE BASE

Procedure and Materials

(1) Sixteen gore, 1 mil aluminized Mylar film, acetone washed.
(2) Sprayed Dupont 46971, 3-5 mils.
(3) Brushed four 200 gram coats of the following:

	Parts
Epon 872-X-75	100.0
Cab-O-Sil	1.5
PC 1244	.3
Agent U	4.6

(4) Series 1, sample 2, dacron bonded to fourth coat.
(5) Vacuum impregnated with the following:

Gelatin Solids (25%)	300 g.
Water	495
Ethylene Chlorohydrin	315
Methyl Butynol	90
	1200 g.

TABLE 26

COMPOSITE 1, RIGIDIZED AT VIRON 12 MARCH 1965

Time	Chamber Pressure mm Hg	T_1 °F	T_2 °F	T_3 °F
0925	Start Pump	70	68	72
0930	1.00	44	47	72
1030	0.90	80	72	84
1130	0.80	99	84	90
1330	0.55	97	85	89
1430	0.42	101	87	87
1530	0.37	101	87	86
1600	0.30	98	87	85

T_1 Near center of collector

T_2 Edge of fabric near chamber front

T_3 Chamber atmosphere

(6) Rigidization
    (a) 1.3 in. Hg. held on Mylar
    (b) Nearly full cure after 6-½ hours in chamber. Average pressure about 100 microns. Lowest pressure was 4.6×10^{-5}mm Hg
(7) Remarks: Good surface. No creases. See Figure 16. Best surface of the 3 delivered collectors.

Table 27 lists vacuum data for this collector.

c. Composite 3

This composite was assembled with the same materials and amounts as those used in Composite 4. The dacron fabric was impregnated with gelatin at Viron on 12 March 1965. The impregnated composite was then packaged and was to have been cured at Wright-Patterson the following week. However, it was discovered that the aluminized Mylar film had become loosened from the flexible layer possibly due to attack by organic solvents contained in the gelatin solution.

d. Composite 4

RIGIDIZED 16 MARCH 1965 AT WRIGHT-PATTERSON AIR FORCE BASE

<u>Procedure and Materials</u>

(1) Sixteen gore, 1 mil aluminized Mylar, acetone washed.
(2) Fabrication pressure 1.00 in. Hg.
(3) Sprayed Dupont 46971, 3-5 mils.
(4) Sprayed two coats of the following:

	Parts
Epon 872-X-75	300.0
Beetle 216-8	10.1
MIBK	62.1
Polysolve	61.2
Xylol	61.2
Cab-O-Sil	5.7
	500.3
Agent U	13.7

(5) Series 1, sample 2, dacron bonded to second coat of No. 4.

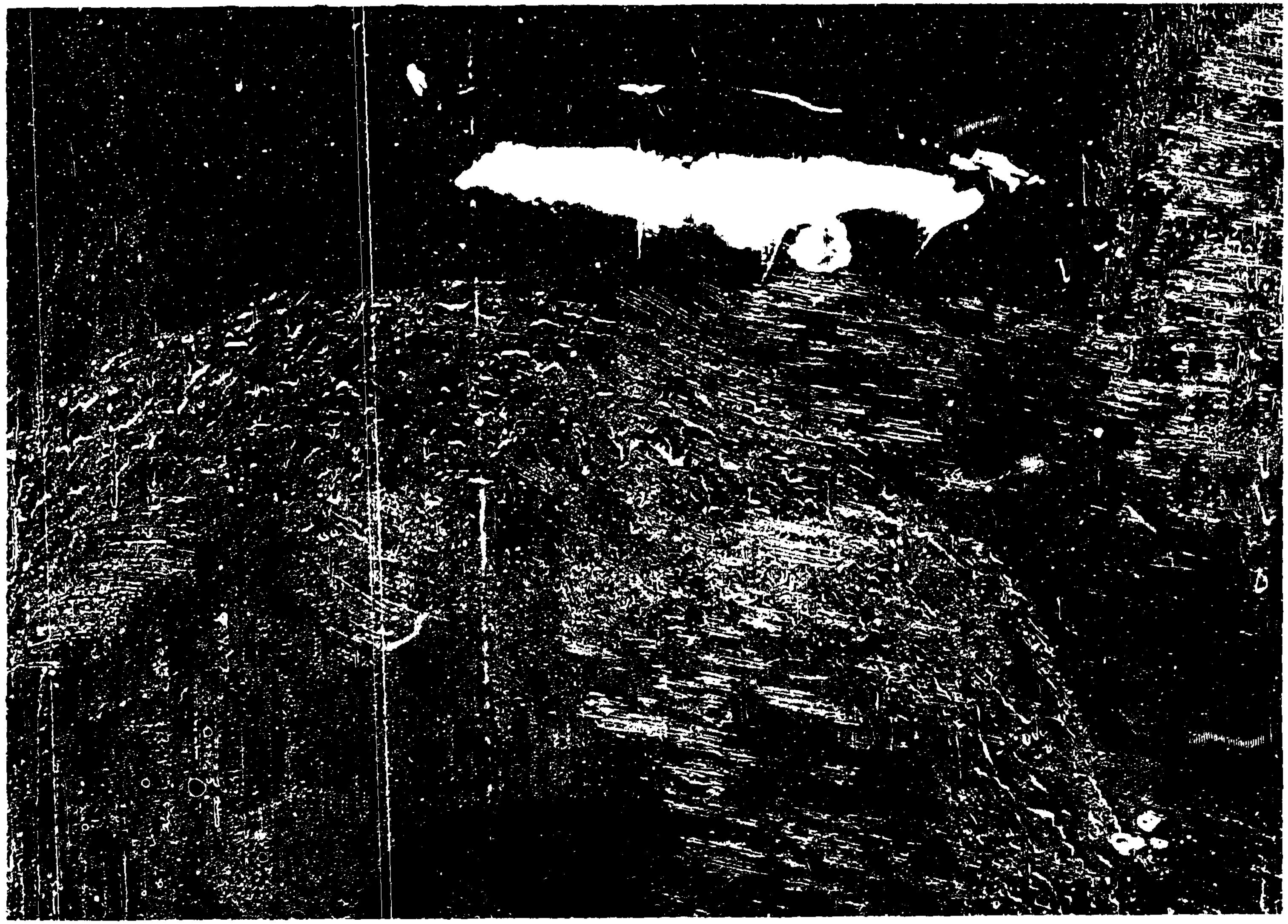

Figure 16 - Vacuum Cured 2-½ Ft Diameter Solar Collector Model

TABLE 27

COMPOSITE 2, RIGIDIZED AT WRIGHT-PATTERSON 17 MARCH 1965

Time	Chamber Pressure mm Hg	°F				
		T_2	T_3	T_4	T_5	T_9
1025	Started Pump	60	60	60	60	67
1030	0.40	30	30	32	50	72
1130	0.17	77	77	82	82	96
1200	Roughing pump stopped. Cleaned trap.					
1205	Started pump					
1227	Closed off chamber vent. Checked pump.					
1232	Opened vent to pump.					
1233	0.40	76	75	75	84	93
1250	0.15 Cold wall on.					
1300	0.13 Diffusion pump on.					
1340	1.4×10^{-4}	80	78	50	78	
1430	7×10^{-5}	80	76	52	75	85
1545	4.8×10^{-5}	85	77	58	82	90
1600	4.6×10^{-5} Cold wall off.					
1622	4.6×10^{-5} Diffusion pump off.					
1700	0.70	83	76	70	85	95
	Vented chamber and removed collector.					

T_2 - Edge of fabric near front cold wall, Right.
T_3 - Edge of fabric near front cold wall, Left.
T_4 - Edge of fabric near rear cold wall, Left.
T_5 - Edge of fabric near rear cold wall, Right.
T_9 - Chamber atmosphere above collector center.

(6) Vacuum impregnated with the following:

Gelatin (25%)	450 g
Water	742
Ethylene Chlorohydrin	473
Methyl Butynol	135

(7) Rigidization
   (a) 1.25 in. Hg. on Mylar
   (b) Not fully cured after 6 hours at 200 microns. Fully cured (rigid) after additional 16 hours at about 500 microns.

(8) Untrimmed 28" diameter weight 1250 g.

Table 28 shows vacuum data for this collector.

5. Effect of Heating the Reflective Surface After Cure

It was found that heating the reflective surface of a cured collector produced changes which seemed to eliminate a great deal of the smaller imperfections in the film. At first, a portion of the aluminized film of a collector was heated to about 200°F with a heat gun. A change took place almost immediately which probably resulted from a slight shrinkage in the Mylar but did not seem to affect the bond with the flexible layer. Based on this observation an attempt was made to heat an entire collector. At 180°F the entire surface seemed to smooth out but the contour of the collector became distorted due to the softening of the gelatin.

To avoid overheating the back side of the structure, a bank of infrared heat lamps was directed at the reflective surface of another collector. After several hours, many of the small imperfections were removed due to film shrinkage, however, no significant improvement resulted after several days of continuous heat. It is possible that the Mylar film did not reach a sufficiently high temperature because of reflection from the aluminized surface.

TABLE 28

COMPOSITE 4, RIGIDIZED AT WRIGHT-PATTERSON 16 MARCH 1965

Time	Chamber Pressure mm hg	^{o}F T_2	T_3	T_4	T_5	T_6
0950	Start pump	55	57	57	57	60
1000	0.20	16	16	16	16	50
1030	0.13	38	42	60	45	75
1100	Cold wall on. Diffusion pump on.					
1200	0.20	56	52	65	60	70
1210	All systems off. Cleaned cold trap. Changed oil.					
1230	0.25					
1330	Opened chamber to roughing pump. Cold wall on.					
1400	1.0 - 0.25	62	57	75	67	80
1500	0.17	43	43	62	52	60
1600	.18 Cold wall off, vented chamber, removed collector.					
1630	Replaced collector in chamber. Started roughing pump. Heat lamp off.					
3-17-65						
0800	0.50 Removed collector.					

T_2 Right edge of fabric near front cold wall.
T_3 Left edge of fabric near front cold wall.
T_4 Left edge of fabric near rear cold wall.
T_5 Right edge of fabric near rear cold wall.
T_9 Chamber atmosphere above collector center.

SECTION 5

CONCLUSIONS

1. Attempts at chemical modification of gelatin to produce a vapor catalyzed system resulted in decreased physical strengths.

2. Chemical modification of gelatin resulted in less soluble products.

3. Rigidization of plasticized gelatin laminates in a vacuum exhibited considerably lower flexural strengths than laminates that were pressure and heat cured.

4. A gelatin-plasticizer formulation, suitable for vacuum impregnation at room temperature, was developed and utilized to rigidize expandable, honeycomb-type structures via plasticizer boil-off.

5. A gelatin solution viscosity of from 500 to 1000 centipoises is necessary for vacuum impregnation in a minimum length of time.

6. Gelatin-rigidized structures were reflexibilized with steam, however, full inflation of structures during the second cure cycle did not occur primarily due to gelatin drainage and fabric porosity.

7. An improvement of the solar collector Mylar - flexible layer bond was obtained by utilizing an adhesive tie coat.

8. The small crease lines which slowly developed on nearly all of the solar collector reflective surfaces probably were caused by solvent attack resulting in loosening the Mylar - flexible layer bond.

9. During the study of collagen it was observed that:

    a. Oriented, uniform films could not be obtained from native collagen from hides. This was primarily due to the lack of proper processing equipment. Therefore, physical strength data for these films was not meaningful.

    b. Physical strength data for collagen films obtained from commercially available sausage casings gave uniform strengths, somewhat superior to strengths of gelatin alone.

    c. Attempts to saturate native or commercial collagen films with gelatin did not produce increased strengths, because of lack of gelatin penetration into the collagen and lack of adhesion.

d. Various curing or cross-linking agents did not result in increased strengths for either native or commercially prepared collagen films.

e. Dispersing commercial collagen cords in gelatin followed by twisting and drying under tension did produce markedly superior tensile strengths.

SECTION 6

RECOMMENDATIONS

1. Gelatin-plasticizer combinations which will result in higher gelatin concentrations and viscosities amenable to room temperature vacuum impregnation should be further investigated.

2. Vacuum impregnation of high solid content gelatin solutions at elevated temperatures should be optimized.

3. The solar collector flexible layer should be further developed.

4. The effect of gelatin solvents on the flexible layer should be determined.

5. Gelatin should be used to rigidize larger structures.

APPENDIX A
IMPROVEMENT OF GELATIN FOR RIGIDIZATION OF EXPANDABLE HONEYCOMB STRUCTURES

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Swift and Company
Chicago, Illinois

A. OBJECTIVES

The objectives of this research effort were as follows:

1. Investigation of solvent-plasticizer systems for gelatin and certain of its derivatives.

2. Formulation of such systems under (i) above, which would permit saturation of a fabric base so as to yield a flexible material capable of rigidizing through evaporation of the solvent-plasticizer in a space environment.

3. Selection of that system of solvent-plasticizer which, when rigidized as a supported or non-supported film, would yield maximum strength to the saturated fabric.

4. Manufacture and delivery of required amounts of accepted formulation to the prime contractor for evaluation and use.

B. CONCLUSIONS

Several general conclusions may be drawn as a result of the experimental work completed under this contract.

1. The highest film tensile strengths obtained were those of unmodified gelatin films cast from aqueous solutions only.

2. Cross-linking by heat or chemical treatments weakened the gelatin film from 10% to 20%.

Additional conclusions which may be tentatively drawn, based on incomplete work, are listed below. These are best described as indications because the data is limited and adequate duplications were not run.

1. Dialysis of the gelatin even at 70°F does not remove sufficient low molecular weight materials to affect a measurable improvement in tensile strength.

2. The weakening effect of cross-linking techniques increases in the order of heat < formaldehyde < epichlorohydrin < glutaraldehyde < glyoxal

3. Carbamidation, deamination, and polymerization with cyanamide result in less weakening than the cross-linking reactions.

4. Deaminated gelatin and gelatin polymerized with cyanamide was strengthened by cross-linking with epichlorohydrin and glutaraldehyde but weakened by formaldehyde or glyoxal.

C. EXPERIMENTAL

All of the work done with gelatin as the resin system was carried out using an acid-cure pork skin gelatin manufactured by Swift and Company at their Kearny, New Jersey, plant. In order to facilitate making up the various solutions formulated without the problem of air incorporation, Swift and Company prepared and supplied to all sub-contractors and Viron approximately 1400 lb of gelatin jelly which required only melting. This product analyzed as follows:

300 gram Bloom gelatin	38.0%
Water	61.8%
Hydrogen peroxide	0.1%
Propionic acid	0.1%

The pH of this product was 4.5.

Due to the undesirability of using pentachlorophenol in a food plant, hydrogen peroxide was employed to kill bacteria and propionic acid to retard mold. Mold growth was not prevented and the material required freezing or drying to preserve it. In addition, the molded portion of the gel was replaced by dry gelatin of the same quality.

1. Solvent-Plasticizer Systems Studied

All conventional peptizing agents normally used to liquefy gelatin gels are believed to be relatively non-volatile, e. g. calcium chloride, calcium nitrate, magnesium chloride, zinc chloride, sodium B-napthalene sulfonate, urea, thiourea, and ammonium thiocyanate. The last three, however, will dissociate into volatile components under intense vacuums.

Saturation techniques as applied to the woven fabric base materials give rise to a secondary problem of air entrainment, and in the case of gelatin, this is a cause of serious foaming and a resulting weakened film. Therefore, a defoaming agent was a definite requirement. Fortuitously, these requirements, namely, volatile liquefier and volatile defoamer were met with ethylene chlorohydrin and methyl butynol respectively, so that these two materials were employed with water in the first system studied.

Plasticization is effected primarily by moisture held in the film or by hygroscopic materials which hold moisture within the film. Therefore, the incorporation of moisture or any volatile humectant that is retained by the film until rigidized would appear to serve as a suitable plasticizer.

Therefore, the major study was on a system for dissolving gelatin which comprised as solvents:

a. Water as the primary solvent,

b. Ethylene chlorohydrin as a liquefier, and

c. Methyl butynol as a cosolvent and defoaming material.

Several drawbacks to the use of such a system were anticipated:

a. Some reaction of the ethylene chlorohydrin with the other components including gelatin and water with some formation of HCl, ethylene glycol, and/or hydroxyethylated gelatin.

b. Due to the liquid consistency, there would be a definite tendency to run or concentrate non-uniformly over the fabric.

c. A possibility of degradation of the film strength if the liquefied solution was aged for any length of time prior to use.

To determine proper perspective of these disadvantages, a study was made of a system containing these ingredients and the changes that took place when allowed to stand at two different temperatures. Three series of samples were set up. The first contained equal weights of gelatin, ethylene chlorohydrin (ECH) and water; the second substituted methyl butynol (MB) for the ethylene chlorohydrin; and the third used 50-50 ECH and MB as the replacement for ECH and MB. Each sample was subdivided into several lots and the pH of each lot varied from 4.2 to 9.0. Another set was divided into two series; one held at ambient room temperature (25-30°C) and the other at 50°C.

Periodically samples were withdrawn, diluted to a standard 6-2/3% gelatin solids, and run for jelly strength (Bloom) and viscosity (mp). The pH was also checked to determine whether hydrolysis or reaction with ECH had taken place.

Numbers used to designate the curves shown in Figures 1 through 6 refer also to the formulations used in this study as follows:

Formulation	Contents
1, 4, 7, & 10	33.3% Gelatin 33.4% Water 33.3% Methyl Butynol
2, 5, 8, & 11	33.3% Gelatin 33.3% Ethylene Chlorohydrin 33.4% Water
3, 6, 9, & 12	33.3% Gelatin 16.6% Methyl Butynol 16.7% Ethylene Chlorohydrin 33.4% Water

In Figure 1, it is clearly indicated that there was a slow reaction of ethylene chlorohydrin with the gelatin at room temperature. In fact, it was negligible unless a slightly alkaline condition prevailed. Figure 2 indicates the same trend, but at much faster rates at the higher temperature (50°C) From this study, it was concluded that the use of a gelatin solution liquefied with ethylene chlorohydrin could be used promptly without fear of a secondary reaction, particularly in acid solution. Storage prior to use would result in a gradual breakdown.

The effects of these variations in solution composition at two temperatures (25 and 50°C) upon gel strength and viscosity are shown in Figures 3 and 4. The effects upon viscosity are shown in Figures 5 and 6. Although all this data confirms a definite reaction of ethylene chlorohydrin with gelatin and/or water, it equally suggests that ethylene chlorohydrin would be most suitable to aid in saturation of fabrics with liquefied gelatin. This is based upon the slowness of the reaction and the possibility that all of the liquefier would be removed prior to storage of the finished structure in its final compact form.

In general, it is known that proteins are insoluble in all anhydrous solvents. Certain polyhydric solvents, containing at least some hydroxyl functions are compatible with gelatin

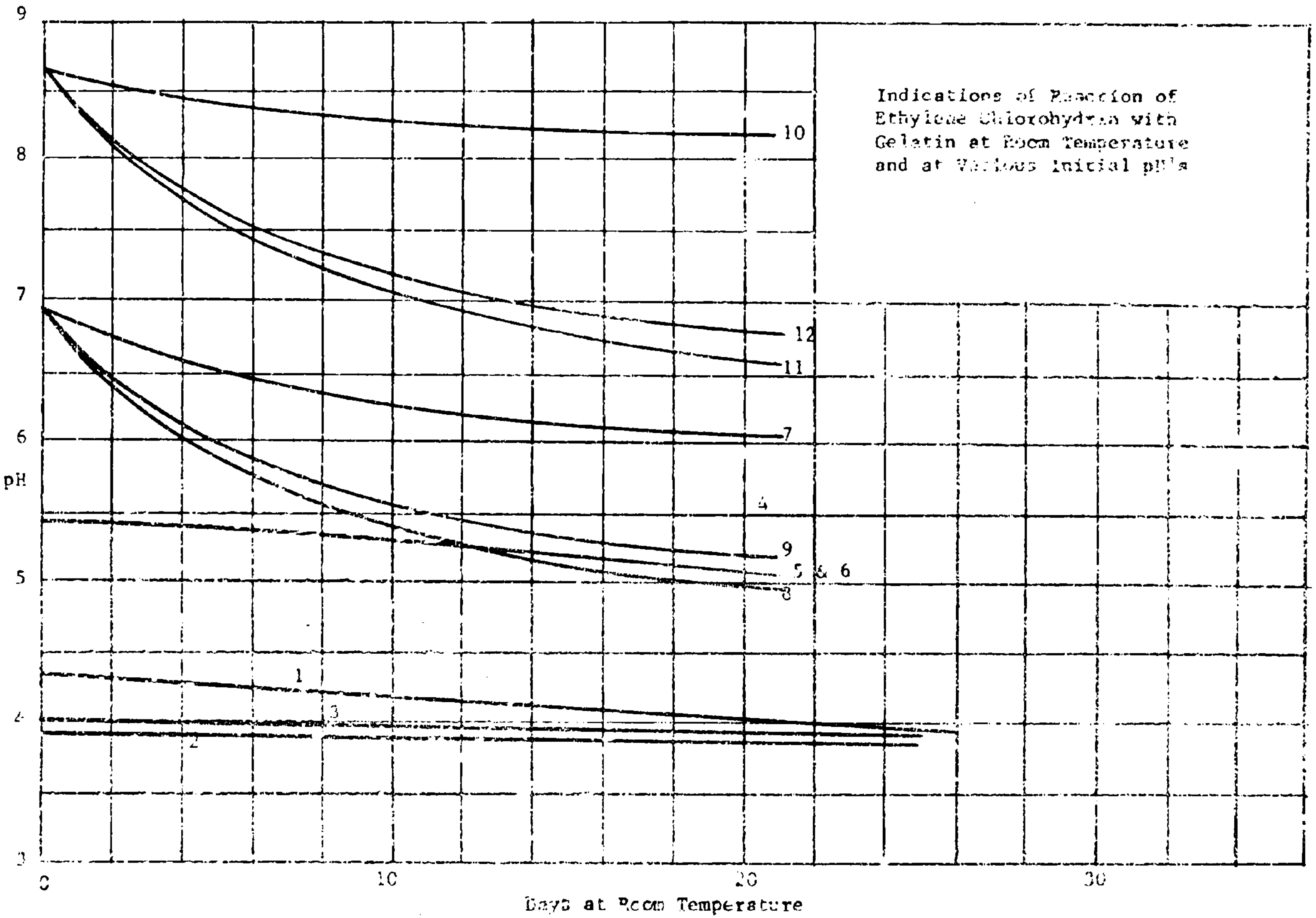


Figure 1
Ethylene Chlorohydrin Reactions with Gelatin at Room Temperature

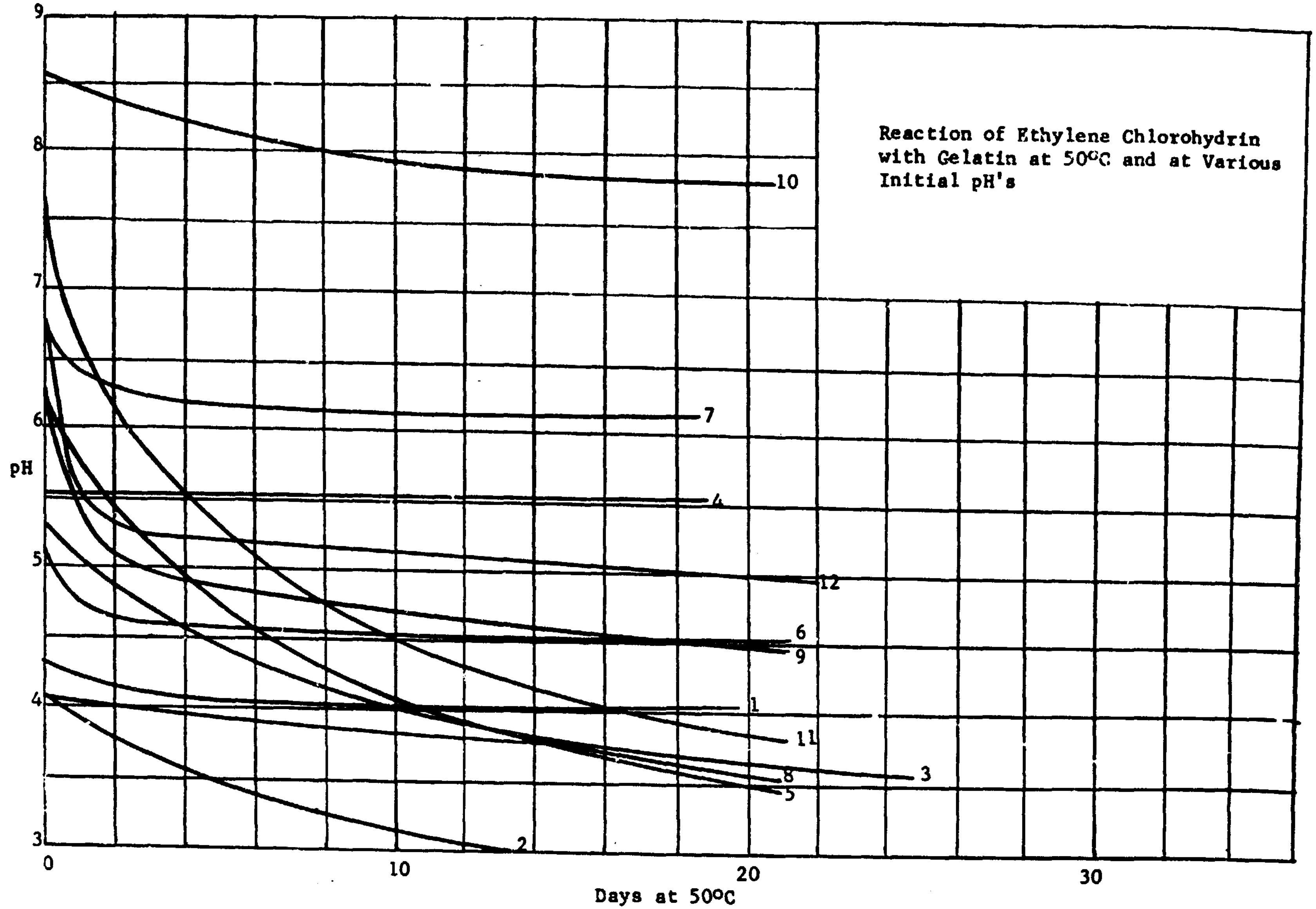


Figure 2
Ethylene Chlorohydrin Reactions with Gelatin at 50°C

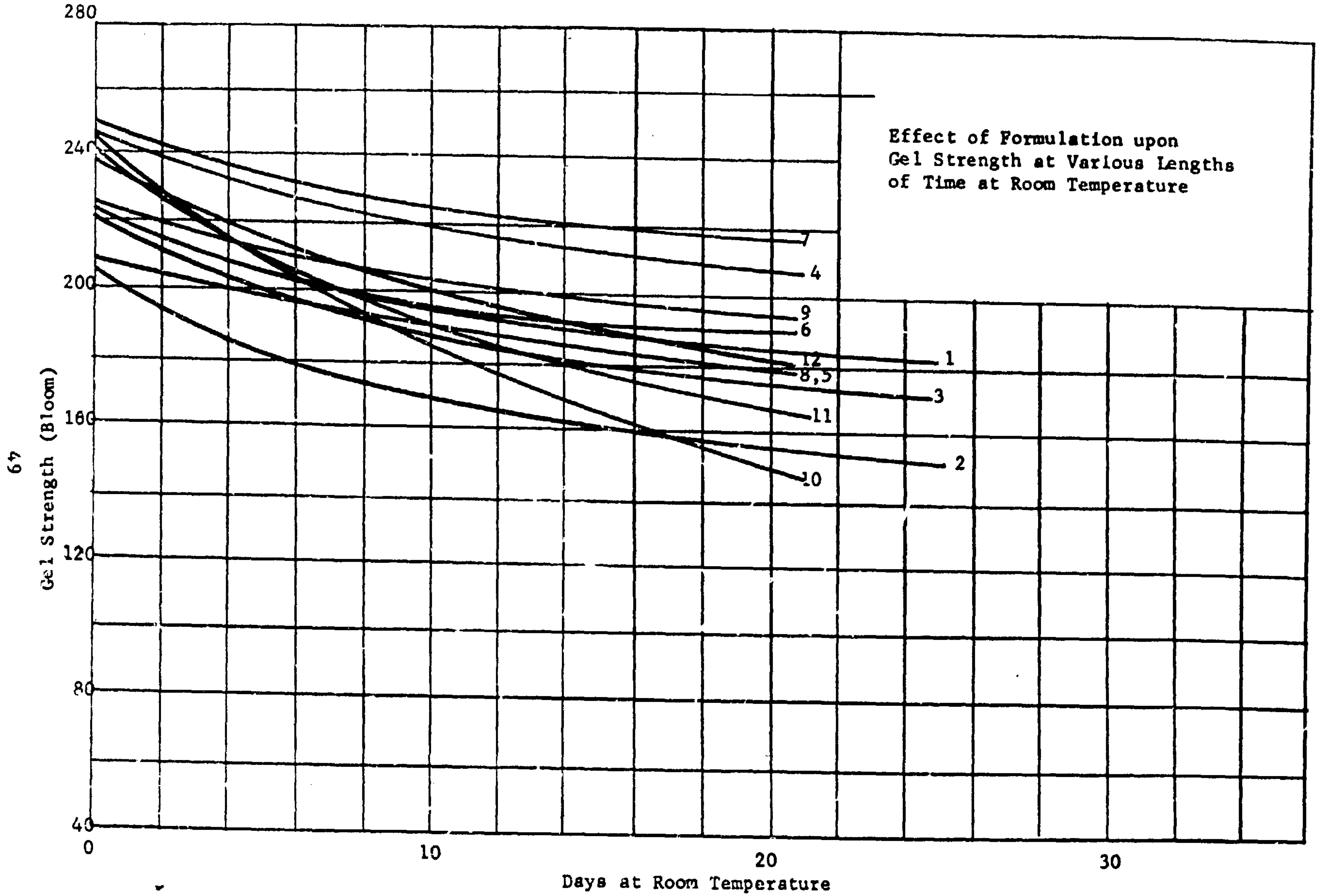


Figure 3
Gel Strength Variation with Time at Room Temperature

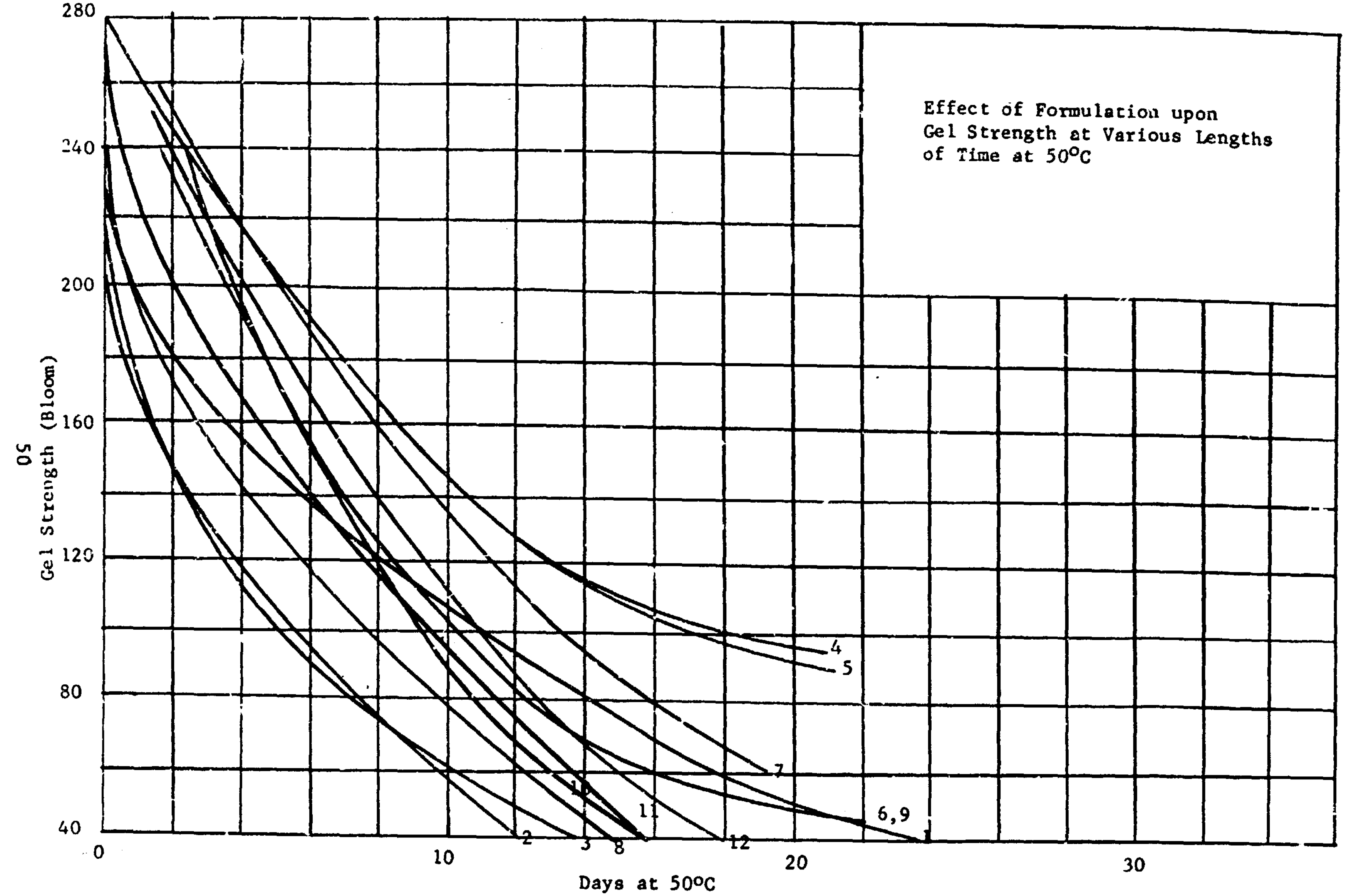


Figure 4
Gel Strength Variation with Time at 50°C

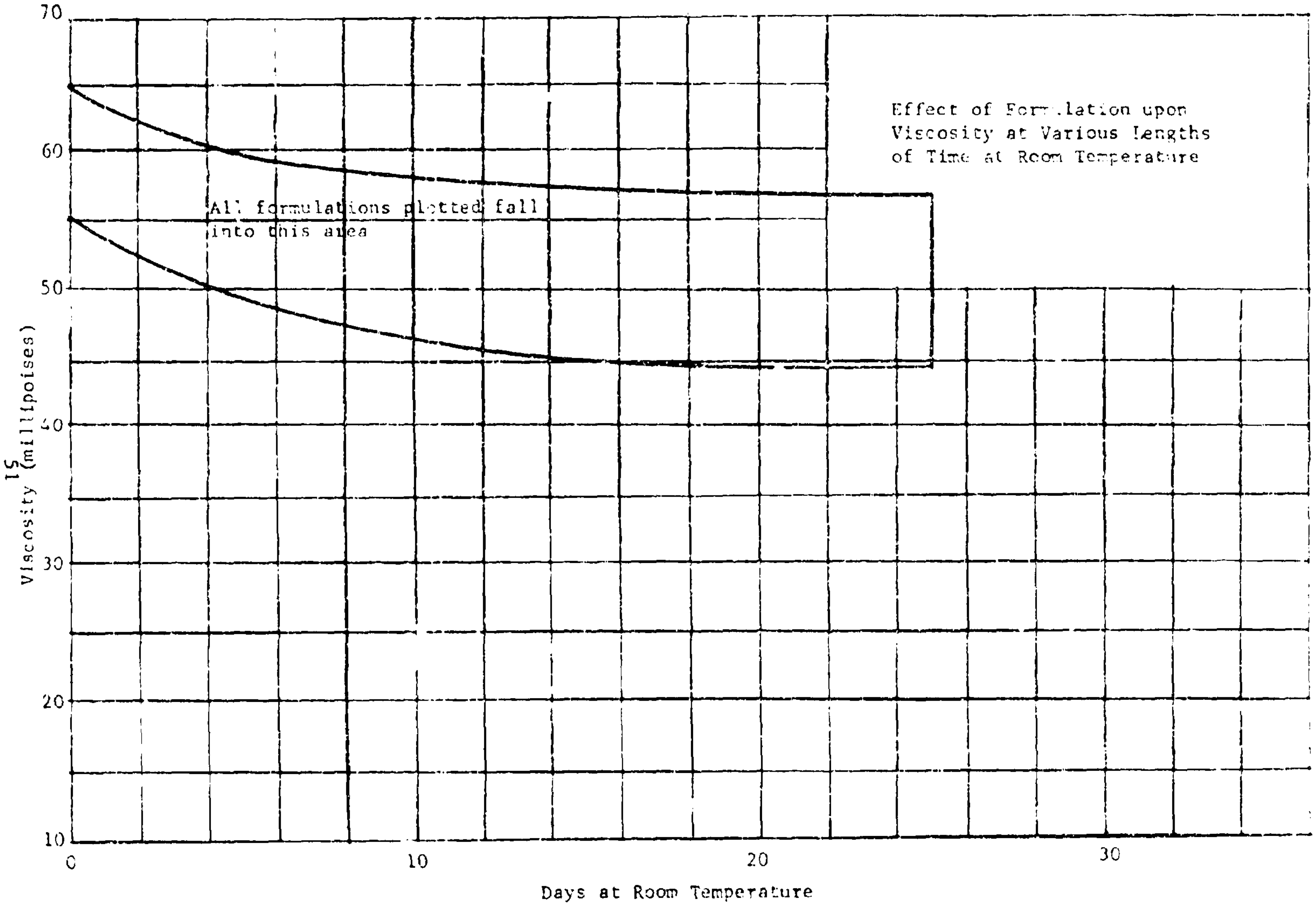


Figure 5
Variation of Viscosity with Time at Room Temperature

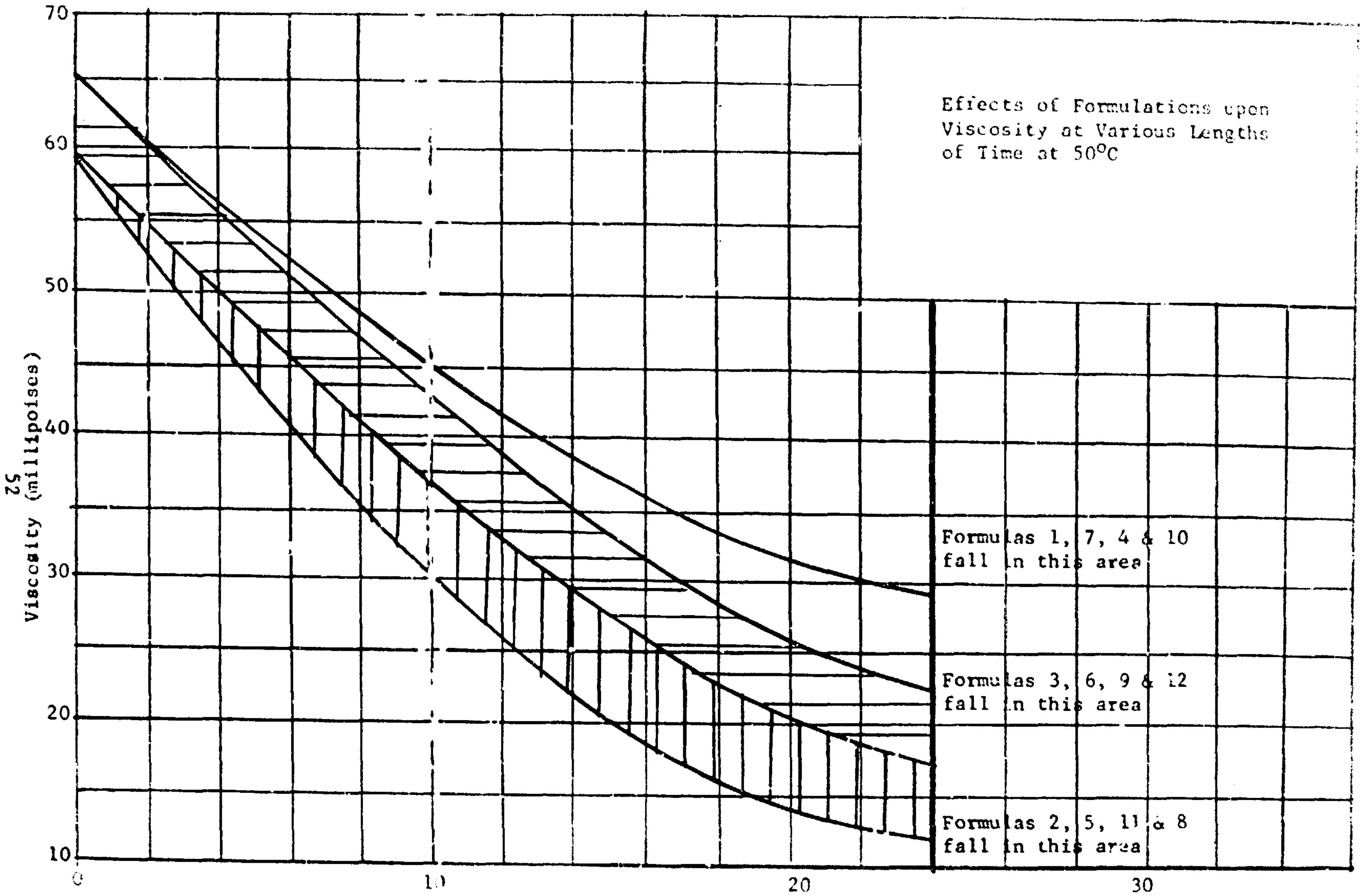


Figure 6
Variation of Viscosity with Time at 50°C

in the presence of some moisture and those that are hygroscopic and non-volatile are quite efficient as plasticizers. Therefore, it was accepted that moisture is the true plasticizer and when present in gelatin films to the extent of approximately 30% it provides adequate flexibility for bending and folding.

2. Effect of High Vacuum upon Supported Gelatin Films

	I	II
Gelatin	40%	40%
Water	20%	30%
Ethylene Chlorohydrin	28%	20%
Methyl Butynol	12%	20%

Various techniques for saturation of the glass fabric were employed, and some modifications of the formulation were tried. The above two formulations which differ substantially only in the ratio of water to organic solvent best saturated the fabric. This was improved even further by pre-wetting the fabric in the solvent mixture alone (minus the gelatin) prior to saturation.

In all, nine variations were made and one set each was sent to WPAFB and to Viron. After 30 days at high vacuum the samples were removed by WPAFB and Viron personnel and tested. All specimens appeared to undergo little change after the 30 days in high vacuum.

The specimen which was found to be the best of the lot had been prepared by Swift as follows: The second formulation was prepared in sufficient volume to permit complete submersion of the fabric at room temperature with sufficient time for complete escape of air bubbles. All foam was removed by skimming prior to withdrawal of the fabric. The saturated fabric was withdrawn and placed upon Mylar laminated to a level glass plate. This was then recoated with the same solution and leveled with a Bird applicator to a uniform thickness. When dry it was removed from the plate and sent to WPAFB and Viron. The general conclusion drawn was that high vacuum in itself would not deteriorate supported gelatin films in 30 days at ambient temperatures.

3. Preparation of Gelatin Derivatives

Known reactions of amino functions suggested several procedures for modifying the gelatin molecule, all of which have been studied by Swift personnel at one time or another. Several of these were believed to offer possibilities as high strength films whether or not subsequent cross-linking reactions were carried out.

a. Heat

It has been established that excessive temperatures effect major changes in the gelatin structures. The critical temperature appears to be about 35°C, the transition temperature of alpha and beta forms. This means that the drying of gelatin above this transition point produces the alpha form whereas the beta form results at lower temperatures. The significant feature is that the beta form will show 10-20% higher tensile strength figures than the alpha gelatin. This same loss of strength is magnifested by heating dry gelatin films and should be borne in mind when interpreting tensile strength figures for any specimen.

b. Peptizing Agents

In addition to the use of ethylene chlorohydrin, which is unique because it is volatile, other chemicals known to have the property of depressing gelation were studied. Thiourea and ammonium thiocyanate which dissociate at low temperatures into volatile components were also studied. No vacuum condition approaching that required could be obtained so all the test specimens were weak due to incomplete drying. It was concluded that the use of these liquefiers immediately after formulation does not inherently weaken the film since removal by dialysis results in a film approximately as strong as the gelatin control. However, any storage of such liquefied gelatin preparations even at room temperature for more than several days resulted in a gradual, but definite, degradation of the gelatin micelle as evidenced by the viscosity drop in the solution. Commercial liquid animal glues have manifested this same drop in viscosity with corresponding decrease in shear strengths as measured for adhered hard maple blocks. It has also been established that this drop in molecular size or degradation is not conventional hydrolysis caused by chemical or microbiological agents because there is practically no increase in the Van Slyke or Sorenson titrations indicating the release of amino functions. Rather, it is believed to be due to the rupture of hydrogen bonding with resulting "unwinding of the coil".

c. Carbamidation of Gelatin

This reaction can be effected by means of nitrourea or potassium cyanate acting upon free amino functions of the gelatin. Both these reagents dissociate or "dearrange" to form free isocyanic acid.

$$NH_2CONHNO_2 \longrightarrow HNCO + NH_2NO_2 \longrightarrow N_2O + H_2O$$

$$KCNO + HCl \longrightarrow HNCO + KCl$$

The isocyanic acid formed immediately converts free amino functions of the gelatin into carbamino groups:

$$RNH_2 + HNCO \longrightarrow RNHCONH_2$$

Since the carbamino group is much less basic than the original amino group, there is a marked shift in the isoelectric point and a change in the manner in which it cross-links with aldehyde tanning agents.

In order to accomplish carbamidation, gelatin solutions in water (20-30% concentration) were adjusted to a pH of 6.0 at 120°F and 2% potassium cyanate, basis weight of gelatin dissolved in water, was added with stirring. After about one hour reaction time, the solution was poured into large trays to a depth of 1/4 inch and chilled to form large sheets of gel. These were peeled from the trays and suspended over rods in a cold water tank where they were bathed in running cold water for about 48 hours. Dialysis was easily effected in this way using the gelatin as its own membrane. When soluble salt was removed to a constant level (48 hrs), the sheets of gel were spread on screens and dried by passing cool air over the films. Complete drying was effected in about 48 hrs. The gelatin derivative was then ground and stored.

The second sample of carbamidated gelatin, No. 13 on Table 1, encountered overheating and showed about 1/2 the usual strength.

d. Deamination of Gelatin

Conversion of amino functions to hydroxyl groups was accomplished by reaction with nitrous acid as generated from soluble nitrite salt:

$$R{-}NH_2 + HONO \longrightarrow ROH + N_2 + H_2O$$

In this reaction all terminal primary amino and amido functions are converted to hydroxyl groups: e.g., terminal - NH_2 becomes -OH and $-CONH_2$ becomes -COOH. This reaction too causes a marked change in the isoelectric point and in addition changes drastically the manner in which the protein reacts with aldehyde cross-linking agents.

Deamination was effected by adjusting the gelatin solution (20-40%) at 120°F to a pH of 6.0. Then 2% sodium nitrite, basis the weight of gelatin, was dissolved in a 20% aqueous solution and added slowly with stirring. Slow evolution of nitrogen without odorous oxides of nitrogen indicated that the deamination was proceeding smoothly. At the end of gas evolution, the solution was poured on trays and chilled to gelled sheets about 1/4-inch thick. These were dialyzed as described for carbamidated gelatin and finally dried and ground.

c. Polymerized Gelatin (reaction with hydrogen cyanamide)

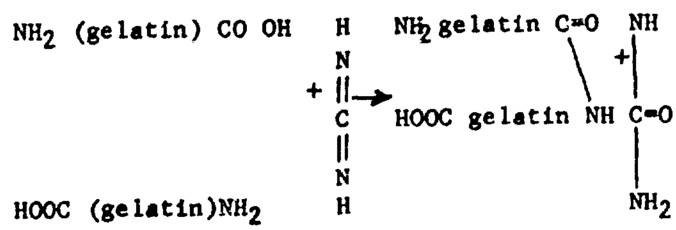
Cyanamide is theoretically tautomeric with carbodimide:

$$NH_2{-}C \equiv N \longrightarrow HN{=}C{=}NH$$

In this form it adds moisture to form urea and thereby chemically promotes a number of reactions which require elimination of water, e.g., esterification, amidation, etc.

$$HN{=}C{=}NH + HOH \rightarrow \underset{H}{HN}{-}\underset{OH}{C}{=}NH \rightleftharpoons NH_2{-}\underset{O}{\overset{\|}{C}}{-}NH_2$$

The suitability of hydrogen cyanamide is based upon its conversion to urea through withdrawal of water from two or more molecules of the gelatin. This may be schematically presented as follows:



While no direct proof of structure was carried out, urea has been found in the reaction mixture and after drying at elevated temperatures the polymerization was manifested by insolubility of the reacted gelatin. The procedure for preparing this derivative should be based upon the use of the finished reaction product within a reasonable length of time. Drying produced an insoluble but moisture-sensitive product and the prepared material remained as a solution for several hours before the viscosity thickened to an unusable state.

To prepare this product, a 35-40% gelatin solution was made in the usual way at an ambient pH of 5.0. It was warmed to 120°F to effect solution and 5% hydrogen cyanamide, basis gelatin weight, was added with stirring. The final solution was used immediately since insolubility took place upon standing or drying. No visible difference was apparent in the final product whether the reaction proceeded for 1/2 hr or 2 hr except for some differences in film strength after cross-linking.

f. Dialyzed Gelatin

In an effort to determine whether stronger films could be produced by removal of lower molecular weight fractions, dia ysis rather than fractional precipitation with acetone or alcohol was preferred since secondary denaturation reactions may have taken place. The procedure used comprised the preparation of gelled sheets about 14 x 20 inches. Those were folded over rod supports and immersed in circulating water at the desired temperature. Although the bulk of soluble ions could be removed by using tap water at the beginning, the process could be completed by several changes of distilled water until no change in the chloride concentration was evident. The gelled protein was finally dried in cool air and ground. Three temperatures of dialysis water were studied since it was expected that dialyzing gelatin at 70°F would extract more of the lower molecular weight components than dialyzing at 35°F. Tensile strengths as determined on the Instron machine are given in Table 1.

g. Effect of Cross-Linking Agents

Although a number of heavy metal salts may be used to advantage in the cross-linking reaction, certain aldehydes were studied because of their greater flexibility, reactivity, and lighter weight. Those studied were formaldehyde, glutaraldehyde, glyoxal, and epichlorohydrin. In every case special techniques had to be developed for their use. None of these could be incorporated into the liquid gelatin without the possibility of premature gelling. If lower concentrations were used, there was a definite uncertainty as to the completion of the reaction within a reasonable period of time. Therefore, all aldehydes were painted on the gelled film prior to drying to insure complete reaction by the time the film had been dried. An exception was epichlorohydrin, which was insoluble in water. Direct application of this by painting or dipping did not guarantee any cross-linking. Since methyl butynol is a compatible coupling agent, and since the reaction of epichlorohydrin with gelatin does not take place immediately, 1% epichlorohydrin basis gelatin was added as a 10% solution in methyl butynol. This was stirred until uniform and it permitted ample opportunity to cast a film prior to gelation.

4. Determination of Tensile Strengths of Unsupported Films

All specimens were cut by means of a die in a laboratory Carver press to minimize shattering. Wherever possible, test specimens were cut prior to complete drying so as to produce smooth edges. Final drying was effected by total evacuation in a chamber at 40 microns and at room temperature. Prior to testing, each specimen was conditioned for 48 hrs at 72-74^{o}F and 50% relative humidity.

Thin film tensile tests were made using dumb-bells ranging in thickness from .01 to .02 inches and at an Instron separation rate of .05 inches/min. No laminated specimens were made for testing. All tensile strength results are shown in Table 1 and are averages for five test specimens.

5. Collagen Films

The very high tensile strength figures alleged for collagen have been obtained on a very specific type of collagen fiber found in tendons but not in skin or bone collagen. Commercially extruded collagen films normally used as sausage casings were washed and dried under tension so that test specimens could be cut. Both had

TABLE I

TENSILE STRENGTHS FOR ALL SPECIMENS

Sample No.		PSI
1	Gelatin control	12000
2	Gelatin control heated dry at 80°C for 4 hrs	10000
3	Gelatin liquefied with ethylene chlorohydrin and aged 3 months	4500
4	Gelatin cross-linked with formaldehyde	10600
5	Gelatin cross-linked with glyoxal	6100
6	Gelatin cross-linked with glutaraldehyde	9100
7	Gelatin cross-linked with epichlorohydrin	10000
8	Gelatin dialyzed at 32°F	10600
9	Gelatin dialyzed at 52°F	11900
10	Gelatin dialyzed at 70°F	11200
11	Gelatin undialyzed control	11000
12	Carbamidated gelatin	11000
13	Carbamidated gelatin (overheated)	6100
14	Carbamidated gelatin #13 cross-linked with formaldehyde	8700
15	Carbamidated gelatin #13 cross-linked with glyoxal	9100
16	Carbamidated gelatin #13 cross-linked with glutaraldehyde	10100
17	Carbamidated gelatin #13 cross-linked with epichlorohydrin	5300
18	Deaminated gelatin	10500
19	Deaminated gelatin cross-linked with formaldehyde	9700
20	Deaminated gelatin cross-linked with glyoxal	7000
21	Deaminated gelatin cross-linked with glutaraldehyde	10200
22	Deaminated gelatin cross-linked with epichlorohydrin	11100
23	Gelatin polymerized with cyanamide	10600
24	Gelatin polymerized with cyanamide and cross-linked with formaldehyde	9650
25	Gelatin polymerized with cyanamide and cross-linked with glyoxal	7400
26	Gelatin polymerized with cyanamide and cross-linked with glutaraldehyde	11000
27	Gelatin polymerized with cyanamide and cross-linked with epichlorohydrin	10100
28	Collagen extruded film (Devro) 1 mil thick	6000
29	Collagen extruded film (Brechteen) 3-4 mil thick	11300

been cross-linked; one with formaldehyde and smoke and the other with aluminum salts. These are listed in Table 1 as samples Nos. 28 and 29, respectively. It was assumed that No. 28 lost about 10-20% of its tensile strength because of cross-linking. The parent film might well have shown a strength of 14,000 or 20% better than the gelatin control.

APPENDIX B

GELATIN APPLICATIONS FOR SPACE STRUCTURES

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A. OBJECTIVES

1. To investigate and develop suitable plasticizer systems to permit deployment of gelatin composite structures and subsequent rigidization by plasticizer evaporation.

2. To study the use of chemically modified gelatin that will rigidize on command by the use of vapor phase catalysts.

B. CONCLUSIONS

1. Water appears to be the only primary plasticizer for gelatin. Organic "plasticizers" serve only as humectants and are useful for conferring better flexibility and foldability on the gelatin in humid earth environments and for slowing the rate of rigidization in vacuum.

2. The best overall system (19% gelatin, 1.9% Goodrich K 702 polyacrylic acid, 4.3% urea, and 74.8% water plus 1% phenol based on weight of gelatin) does not gel at room temperature, and films made from this solution rigidize rapidly to high-strength products whose moduli of elasticity approach that of unplasticized dry gelatin.

3. A process was demonstrated wherein a 10 x 15 inch closed-end cylindrical shelter prototype was impregnated, folded, and deployed in a vacuum (including inflation of flutes) and rigidized by plasticizer loss.

4. Smooth, highly-reflective surfaces were obtained on gelatin-glass cloth laminates by pressing gelatin films on the laminate's surface. This surface was subsequently metallized by vacuum deposition techniques.

5. Plies of gelatin-impregnated glass cloth were shown to be non-adherent under a low load when stored in a 100% RH chamber for two weeks. Lubricants and parting agents were evaluated but appeared to be unnecessary under the conditions of the test.

C. EXPERIMENTAL

1. Gelatin Solution and Film Studies

a. Effect of Storage

Prior to receiving the standard acid hydrolyzed gelatin f Swift, storage stability tests were run on gelatin solutions (Wilson UCOPCO 2342) stored at ambient temperature and at 60°C. The gelatin solutions were prepared with and without the recommended food grade preservative (1% benzoic acid). The length of time when gelatin solutions could be stored in processing equipment without excessive deterioration of mechanical properties from hydrolysis or microbial attack was of practical interest and importance in the preparation of the films and laminates. Table 2 shows that there was little change in the tensile strength of films prepared from normal or benzoic-acid stabilized gelatin solutions stored for a period of one week at room temperature. All samples of gelatin solution maintained at 60°C showed a decline in strength of films with time. This effect was more rapid and pronounced with the sample containing a preservative. These results suggested that gelatin solutions could be maintained at room temperature and at 60°C for periods up to one week with no serious effect on mechanical properties, provided no acid preservative was used.

b. Comparison of Gelatins

Comparative data was obtained at 25°C and 50% RH on the mechanical properties of two commercial gelatins (Swift and Wilson). Additionally, data was obtained on two samples of Swift gelatin that had been dialyzed to remove the low molecular weight fractions. The results of this work are presented in Table 3.

These results show that there was no significant difference between the tensile strengths of films prepared from Wilson gelatin and the two production samples of Swift gelatin (dry and Hydrogel). However, glass cloth laminates prepared from Swift's dry gelatin were markedly superior in flexural strength to those prepared from UCOPCO gelatin. There was no significant difference between the laminates in modulus of elasticity.

TABLE 2

EFFECT OF STORAGE CONDITIONS ON MECHANICAL PROPERTIES

Duration of Storage	Storage Condition: Without Preservative, Room Temp	Without Preservative, 60 C	With Preservative, Room Temp	With Preservative, 60 C
	Tensile Strength (psi)		Tensile Strength (psi)	
As prepared	13,200	13,100	13,800	13,500
2 hours aging	12,400	12,700	12,300	13,700
4 hours aging	12,600	12,300	11,100	12,200
24 hours aging	12,400	10,000	11,900	8,300
48 hours aging	13,500	12,200	14,600	---
168 hours aging	12,400	11,500	13,300	---

TABLE 3

COMPARISON OF GELATINS FROM DIFFERENT SOURCES
AND MANUFACTURING TECHNIQUES

Description of Gelatin	Films: Tensile Strength psi	Films: Elongation, %	Films: Standard Deviation, psi	Laminates: Flexural Strength, psi	Laminates: Modulus of Elasticity, psi
Wilson UCOPCO Gelatin 23/2	13,000	8.6	790	53,400	2.87×10^6
Swift Dry Gelatin	14,100	8.2	450	68,200	2.82×10^6
Swift Hydrogel Gelatin	13,800	8.2	700	- -	- - - - - -
Swift Dry Gelatin + Ethylene chlorohydrin and Methyl Butynol	3,400	3.32	2100	- -	- - - - - -
Swift Gelatin Dialyzed Neutralized pH 7.0	14,[illegible]00	10.8	520	- -	- - - - - -
Swift Gelatin Dialyzed, no pH adjustment	15,200	8.00	410	- -	- - - - - -

Both samples of dialyzed gelatin gave statistically higher tensile strengths (15,000 vs 14,000 psi) than the undialyzed material. However, it is doubtful the 1000 psi increase would justify the additional cost of the dialyzing process.

c. Shrinkage and Expansion of Gelatin Films

The problem of shrinkage and expansion of gelatin on alternate drying and wetting is one that may affect the design and fabrication of gelatin structures.

It was found that a drawdown (80 mil wet film thickness) of gelatin solution shrank to 10 mils on drying. This was an 87.5% reduction in thickness and volume. However, during drying, the lateral dimensions of the same film shrank only 7.5% in one direction and 9.3% in the other. This film was prepared on a Mylar substrate which separated from the substrate during drying.

Samples of dry gelatin film (1-1/2" x 1/2" x 0.01") were also conditioned at 52, 75, and 100% RH at room temperature until they approached equilibrium conditions. After equilibrium was attained, the samples were placed in a desiccator. The changes in dimension and weight are recorded in Table 4.

All samples gained weight and swelled in one dimension (thickness) when exposed to humid atmospheres. On drying, all samples lost weight and shrank in three dimensions. The sample that was dried after exposure to 100% RH became warped and the lateral dimensions could not be measured.

The results of this work appeared to indicate there was a limit to the amount of water which could be absorbed in unsupported films without causing warping on subsequent drying.

d. Fractionation of Gelatin

Swift Hydrogel gelatin was fractionated by coacervation of gelatin from the aqueous solution by the addition of small increments of warm ethanol. The results of this work are shown in Table 5. The original gelatin had a tensile strength of 13,400 psi. It appeared that fractionation effected no increase in strength. The tensile strengths of the gelatins from the various

TABLE 4

EFFECT OF HUMIDITY ON GELATIN FILMS

Condition of Exposure	Weight gms	Length, in.	Width in.	Thickness in.	Comment
As prepared	0.1690	1-1/2	1/2	0.011	
144 hrs at 52% RH	0.1789	1-1/2	1/2	0.012	
120 hrs in desiccator	0.1554	1-15/32	31/64	0.010	Remained flat
As prepared	0.1659	1-1/2	1/2	0.011	
144 hrs at 75% RH	0.1822	1-1/2	1/2	0.012	
120 hrs in desiccator	0.1530	1-7/16	31/64	0.010	Remained flat
As prepared	0.1824	1-1/2	1/2	0.012	
144 hrs at 100% RH	0.3728	1-1/2	1/2	0.025	
120 hrs in desiccator	0.1680	- - - -	- - - -	0.013	Sample warped on drying

TABLE 5

FRACTIONATION OF SWIFT HYDROGEL GELATIN

[38 gms anyhdrous gelatin (calculated) charged to flask]

Fraction	Weight Recovered gms	Molecular Weight	Tensile Strength psi	Elongation %
unfractionated		81000	12,200	8.7
1	5.15	147000	11,600	2.8
2	15.90	110000	10,800	5.4
3	7.12	94000	13,300	5.1
4	3.90	73000	11,600	4.0
5	8.00	45000	11,900	4.9
6	4.50	--	Did not give a usable film	--
Total	44.57	--	--	--

fractions were remarkably uniform in value, probably an indication of very narrow and uniform molecular weight distribution. The molecular weights of unfractionated gelatin and the several fractions were determined by measuring the viscosities of the gelatin in aqueous salt solution (1.0 M, pH6.4 to 6.5) and by calculating the molecular weight from the log viscosity number. Data for the molecular weight and tensile strength and percent elongation are also included in Table 5. It is apparent from the data that variations in molecular weight within the range encountered in Swift Hydrogel gelatin have little or no effect on the tensile properties of the gelatin. However, it must be pointed out that the higher molecular weight compatible with good processing properties is desirable to improve properties at elevated temperatures since polymer chain scission at higher temperatures may occur.

2. Plasticizer Studies

At the outset of this program one of the objectives was to find primary plasticizers other than water for gelatin. It was conceived that such plasticizers, if found, might be more efficient than water and provide either faster or slower rates of rigidization in a high vacuum environment. It was conclusively established that water is the only primary plasticizer for gelatin among the candidate materials that were tested. Organic plasticizers, which act as humectants, caused more water to be retained in the compositions when stored in ordinary earth environments.

a. Screening

Twenty-three organic compounds were screened for possible use as gelatin plasticizing agents (Table 6). These candidate materials were tested in the following formulation:

	Parts
Swift Hydrogel Gelatin	43.25
Hot water	52.75
Plasticizer Candidate	4.00

Films were cast from the above solution, dried, and Clash-Berg bars (2.5 x 1/4 x 0.01 inch) were cut and tested. All candidate plasticizers were compatible with gelatin except glycine, Armeen 8, and nitrilotriacetic acid. The Clash-Berg bars were evaluated on the basis of weight loss and moduli of elasticity after various periods of storage in a desiccator and

TABLE 6

CANDIDATE PLASTICIZERS FOR GELATIN

Ethylene Glycol	Anhydroenneaheptitol AEH
Sucrose	Glacial Acetic Acid
Dextrose	Triethanolamine
Sorbitol	Ethyl Lactate
Formamide	Furfuryl Alcohol
N-Methyl-Formamide	Morpholine
N-Methyl-Acetamide	Glacial Methacrylic Acid
LA-700	Acrylamide
LA-475	Urea
Voranol CP-260	
Carbowax 200	
Carbowax 600	
Glycerine	
Diethylene Glycol	

under vacuum (5×10^{-5} mm Hg). Samples generally lost weight more rapidly in a vacuum than in the desiccator ($CaSO_4$), which was probably due to volatilization of plasticizer along with water from the sample under the influence of vacuum.

On the basis of low initial moduli of elasticity, (ease of folding and deployment) and high terminal moduli (rigidity), eight candidates were considered most promising and were selected for further evaluation. These plasticizers were:

Glycerine	Anhydroenneahepitol
Diethylene glycol	Urea
Sorbitol	Formamide
LA-475	Acrylamide

The effect of increasing concentrations on the mechanical properties of a gelatin film was measured. All films were made according to the following general formula:

Gelatin	20.0 grams
Water	80.0 grams
Phenol	0.2 grams
Plasticizer	2, 5, 10, 20 grams as required

The results of that work are given in Table 7.

The tensile strength for gelatin films containing 9.1% LA-475 (13,800 psi) and anhydroenneahepitol (AEH: 13,100 psi) was not felt to be significantly higher than that for gelatin alone (13,000 psi). The high strengths of these films at higher plasticizer concentrations indicate that these materials are poorer humectants, and retain less water (primary plasticizer) at the test conditions (25°C, 50% RH).

Only three of the plasticizers tested were compatible at all concentrations. They are AEH, sorbitol and glycerine. Of these, AEH was the poorest plasticizer based on percent elongation. Glycerine was the most efficient plasticizer, but high elongation was obtained with a considerable sacrifice in strength. Sorbitol appeared to be the best compromise candidate, based on a reasonably good elongation (171%) and a good retention of strength ([illegible]00 psi at 50% plasticizer levels).

TABLE 7

EFFECT OF PLASTICIZER CONTENT ON MECHANICAL PROPERTIES OF GELATIN*

(Plasticizer Content Based Total Weight of Non-Volatiles)

Plasticizer	9.1%		20%		33%		50%		Comments
	Tensile Strength (psi)	% Elong.	Tensile Strength (psi)	% Elong.	Tensile Strength (psi)	% Elong.	Tensile Strength (psi)	% Elong.	
None	-	-	-	-	-	-	-	-	13,000 psi 5.5% Elong.
LA-475	13,800	9.0	7,200	16.9	4,800	48.7	-	-	Incompatible at 50%
AEH	13,100	6.5	12,000	7.7	9,000	15.5	2,700	62.7	
Sorbitol	12,800	7.4	6,300	17.1	2,500	48.6	1,400	171.6	
Formamide	11,400	5.2	5,700	11.4	1,100	58.0	-	-	Did not dry properly
Acrylamide	11,100	6.7	6,000	7.9	-	-	-	-	Incompatible above 20%
Glycerine	11,000	6.8	6,100	20.1	1,800	83.5	640	369	
Urea	9,600	8.8	1,700	56.1	-	-	-	-	
Diethylene glycol	7,400	9.5	2,900	48.9	800	204	-	-	Too slow drying at 50%

* Films conditioned at 50% RH and 25°C prior to determining strength

Urea gave very good plasticizing action at low concentrations (56% elongation at 20% plasticizer content), but was not compatible with the gelatin film at higher concentrations. It possessed the additional advantage of retarding gelation of aqueous gelatin solutions.

b. Rate of Gelatin Rigidization in a Vacuum

Of primary importance, in the selection of a gelatin-solvent-plasticizer system for use in a deployable space structure, is the rate at which the gelatin becomes rigid in a vacuum. A test stand was devised which measured the modulus of elasticity while the sample was in a vacuum. Measurements were made as a function of time so the rate of rigidization could be determined.

The modulus was determined in the "as prepared" condition, after conditioning at 100% RH, and at time intervals after placing in a vacuum. The results are in Table 8. All films, (except those containing polyacrylic acid) were made up according to the following formulation:

Gelatin (Swift)	40 grams
Water	160 grams
Plasticizer	10 grams

The film containing polyacrylic acid was made as follows:

Gelatin	38 grams
Polyacrylic Acid (Goodrich K 702)	3.8 grams
Urea	8.6 grams
Water	149.6 grams

These solutions were cast into films, dried and conditioned under 50% RH and 25°C.

The modulus of elasticity of all the samples was markedly reduced after conditioning at 100% RH. After one hour of vacuum exposure, gelatin plasticized with only water recovered 80% of its original modulus and in three hours, recovery was complete. The recovery of original modulus of the samples containing gelatin-water-urea-polyacrylic acid and the gelatin - LA 475 was more rapid than the other samples tested. However, only the former sample approached the end strength of the gelatin plasticized with water.

TABLE 8

RECOVERY OF RIGIDITY UNDER VACUUM EXPOSURE

Gelatin-Plasticizer System	As Prepared Conditioned at 50% RH and 25°C	Conditioned in 100% RH 16 hrs at 25°C	Modulus of Elasticity (psi x 10^4) After Varying Hours In A Vacuum (10-20 Microns, 25°C)								
			1	2	3	4	5	6	7	8	24
Gelatin	94.4	20.0	75.6	85.0	94.4	94.4	94.4	94.4	94.4	94.4	94.4
Gelatin + Urea + Polyacrylic Acid (K 702)	23.95	Too low to measure	21.5	40.0	61.0	74.0	80.0	80.0	80.0	80.0	80.0
Gelatin + LA 475	19.0	7.5	17.8	20.8	22.3	24.3	26.2	27.0	27.6	--	31.2
Gelatin + Diethylene Glycol	7.3	1.6	4.7	8.8	12.1	--	17.3	--	30.3	--	Too high to measure
Gelatin + Urea	6.6	Too low to measure	5.1	7.5	11.25	--	13.2	15.8	17.5	19.7	26.4
Gelatin + Glycerine	3.7	Too low to measure	3.6	4.6	5.5	6.4	7.4	8.3	9.2	10.2	23.4
Gelatin + AEH	43.0	9.2	18.3	25.2	30.2	33.6	35.1	36.8	34.3	37.8	50.3
Gelatin + Sorbitol	14.3	7.3	10.2	12.0	14.3	16.3	18.2	18.9	20.3	21.1	33.0

c. Gelatin Solution Viscosities

Viscosity studies were determined on aqueous gelatin solutions containing 0, 10, 20, 30 and 40% of glycerine or urea. The results of this work were compared to viscosity measurements made on the gelatin-water-ethylene chlorohydrin-methyl butynol solutions. The results of these comparisons are summarized in Table 9.

The gelatin-water system at the level of 30% gelatin solids had the lowest viscosity of the four solvent systems tested. However, it showed signs of incipient gelation in the temperature range 30-40°C (indicated by rapidly increasing viscosity). The gelatin-water-glycerine system had the next higher range of viscosities, but this system, particularly at high concentrations, gelled at higher temperatures than gelatin-water alone.

The gelatin-water-ethylene chlorohydrin-methyl butynol and gelatin-water-urea systems both reduced the temperature at which gelation occurred. However, viscosities were lower with urea. Urea possesses the additional advantage of nontoxicity, while ethylene chlorohydrin is toxic.

d. Peptizing Action of Additives on Gelatin Solutions

The plasticizer candidates previously discussed were tested for peptizing action (inhibition of gelation) on gelatin solutions at room temperature. The test formula was as follows:

Gelatin	20 grams
Water	80 grams
Phenol	0.2 grams
Additive	20 grams

Only solutions containing formamide, glacial acetic acid, morpholine, glacial methacrylic acid, and urea remained fluid at room temperature over a period of 17 days.

3. Gelatin Laminates

a. Effect of Glass Finishing Agents on Laminate Strengths

The effect of nine fiberglass finishing agents on flexural strength was determined on laminates prepared from gelatin and 181 fiberglass cloth. As can be seen from Table 10,

TABLE 9

VISCOSITY OF GELATIN SOLUTIONS

Gelatin Composition	Viscosity (cps) at T°C 60	50	45	40	35	30	20	10
40% Gelatin in water	770	880	980	1,450	4,500	10,000	--	--
30% Gelatin in water	140	170	190	250	420	10,000	--	--
20% Gelatin in water	19	28	35	42	50	62	--	--
10% Gelatin in water	1.2	3.2	4.9	7.2	10	14	--	--
Gelatin in Water-Ethylene Chlorohyrdin-Methyl Butynol								
40% Gelatin	9,200	12,500	14,500	17,000	19,500	23,000	--	--
30% Gelatin	1,600	2,100	2,400	2,700	3,100	3,500	7,600	50,000
20% Gelatin	210	300	350	420	480	580	800	1,600
10% Gelatin	27	37	43	50	58	68	94	130
Gelatin in Water-glycerine								
40% Gelatin 100 water-200 glycerine	1,600	100,000	--	--	--	--	--	--
30% Gelatin 267 water-200 glycerine	530	570	760	1,100	100,000	--	--	--
20% Gelatin 600 water-200 glycerine	56	70	90	130	260	1,000	--	--
10% Gelatin 600 water - 200 glycerine	3.7	5.4	6.6	8.8	11	13.5	21	32
Gelatin in Water-Urea								
28.6% Gelatin 300 water - 200 urea	1,400	1,800	2,000	2,300	2,800	3,800	--	--
20% Gelatin 300 water-100 urea	70	96	110	140	170	220	--	--
10% Gelatin 400 water - 50 urea	1.1	1.3	1.4	1.5	1.6	1.8	2.1	--

TABLE 10

EFFECT OF GLASS FINISHES ON LAMINATE STRENGTH

Finishing Agent	Flexural Strength psi
Volan A	70,900
615	67,300
112	65,800
Neutral pH	63,200
A-1100 hard	58,900
A-1100 soft	57,700
Z-6030	50,600
Garan	31,500
A-172	19,200

Volan A finished glass resulted in the strongest laminate. Volan A is a methacrylic chromic chloride treatment of the fabric. Chromium is a cross-linker for gelatin and probably forms a strong bond between the gelatin and the finishing agent.

b. Temperature Stability of Gelatin Laminates

Temperature stability tests were initiated on gelatin-glass cloth laminates to determine the effects of time and temperature on strength properties. The samples were aged in Labline ovens at 212, 257, 302, and 347°F for periods up to sixteen days.

Aging at 212°F for 16 days resulted in an increase in flexural strength of 5,900 psi above the control, after a slight initial decrease during the first four days. Aging at 257°F for 16 days had no effect on the strength of the laminates after a loss of 4000 psi during the first day. Significant strength losses occurred when the laminates were aged at 302 and 347°F for one week. Table 11 gives further results of these tests.

c. Low Pressure Laminated Five-Ply 181-E Glass

Cloth laminates containing 30% gelatin solids were prepared using only enough pressure during layup to flatten the laminate and squeeze out excess air. The samples were dried under three conditions: (1) ambient temperature and RH for 8 days, (2) four days in a $CaSO_4$ desiccator, and (3) four days at 3×10^{-5} torr. Flexural strengths of the laminates varied from 15,800 to 18,300 psi which is only 1/4 to 1/3 the strengths obtained with high-pressure laminates.

d. Adhesion of Gelatin

(1) Bonding Gelatin to Plastic Films

A glycerine plasticized gelatin laminate with a 3 mil Mylar film on one side and a 3 mil H-Film on the other, was subjected to high pressure. Upon removal from the press, the Mylar peeled off easily although some adhesion was noted. The H-Film adhered tightly and could not be removed. However, after two days in a desiccator, the H-Film was removed without difficulty. It was concluded that the H-Film would not bond to dehydrated gelatin.

TABLE 11

EFFECT OF TEMPERATURE AGING
ON GELATIN GLASS CLOTH LAMINATES

Aging (1) Temp °F		2 Days	4 Days	8 Days	16 Days
212	Flex. Str *	61,500	58,100	61,900	69,400
	Mod. of E.+	2.81	2.88	2.89	2.99
257	Flex. Str.	59,700	58,000	55,000	57,600
	Mod. of E.	2.86	2.83	2.75	2.77
302	Flex. Str.	64,100	57,000	47,200	36,800
	Mod. of E.	2,83	2.73	2.65	2.69
347	Flex. Str.	40,600	30,300	25,400	18,200
	Mod. of E.	2.62	2.54	2.58	2.88

* Flexural Strength (psi) initial value before aging was 63,500

\+ Modulus of Elasticity (psi x 10^6) initial value before aging was 3.04

(1) Tested at Room Temperature

(2) Peel Strengths of Gelatin-Mylar

Gelatin films bonded to aluminized Mylar with a neoprene adhesive were tested for peel strengths as determined by ASTM 903-49. Separations occurred mostly on the Mylar-adhesive interface. Values ranged from 4.8 to 22.5 lb/inch. It was felt that the wide range in the results were due to air entrapment between the Mylar and the gelatin film.

(3) Reflective Surfaces for Gelatin

Several approaches to provide a reflective surface for gelatin were examined during this study. Aluminum and chromium were vacuum deposited on dry gelatin laminates resulting in good reflectivity. The chromium-plated gelatin tarnished slightly when conditioned at 100% relative humidity. Cellophane was bonded to a gelatin laminate at high pressure and vacuum metallized.

The chief disadvantage of aluminizing gelatin laminates by direct vapor deposition or by pressing aluminized cellophane to a laminate was that the fabric pattern "showed through" and gave a diffuse reflectance. Painting, dipping and spraying aluminum pigmented pastes and solutions on gelatin-glass cloth laminates did not produce reflective coatings.

e. Effect of Aging Gelatin Dip Solution on Laminate Strengths

Twenty-five percent gelatin-water solutions were aged at 60°C for periods of 0, 1, 2, and 3 weeks. Glass-cloth laminates were made from each of the four solutions and conditioned 48 hours at 50% RH prior to pressing one-half hour at 130°C and 500 psi. Molecular weight and viscosity determinations were made at the given time intervals.

The data on Table 12 indicates that aging for three weeks at 60°C resulted in some loss of strength, while the molecular weight was markedly reduced. The viscosity of the solution also decreased. Part of the observed loss in strength can be attributed to a lower resin content caused by the reduced viscosity which resulted in increased resin flow out while pressing the laminate.

TABLE 12

EFFECT OF AGING GELATIN SOLUTION ON
GLASS CLOTH LAMINATE STRENGTH

Number of Weeks Gelatin Solution was Aged at 60°C	Molecular Weight	Laminate Resin Content	Flexural Strength psi	Modulus of Elasticity psi x 10^6
0	98,330	33.6	58,900	3.06
1	71,450	28.4	59,900	3.24
2	33,190	25.6	51,200	3.79
3	24,950	22.6	46,100	3.35

f. Self Adhesion of Gelatin-Impregnated Glass Cloth

Tests were run to determine the amount of self-adhesion of glass cloth impregnated with gelatin and gelatin plus plasticizer. All tests were run by stacking the impregnated glass cloth in a humidity cabinet maintained at 100% RH. Two plies of glass cloth containing the same gelatin-plasticizer system were in intimate contact with each other in the stack. Different formulations were separated by wire gauze to facilitate circulation of the damp air through the stack. The following gelatin-plasticizer systems were tested:

Gelatin	Gelatin-formamide
Gelatin-glycerine	Gelatin-urea
Gelatin-diethyleneglycol	Gelatin-AEH
Gelatin-urea-polycrylic acid	Gelatin-LA 475

In addition to testing the various gelatin formulations, the following parting agents were tested: silicone mold-release compound, zinc stearate, Armid O, and neutral oil. After 2 weeks storage at high humidity, no serious self-adhesion was noted for any of the systems tested. This was true for samples containing no parting agent as well as those sprayed with the various mold release compounds listed. All plies could be easily separated with a minimum amount of force.

4. Expanded Structures

The feasibility of opening the flutes in impregnated Raypan using balloons was demonstrated. A panel (6" x 16") of 1/2" Raypan was impregnated with gelatin solution. Prior to impregnation, long, thin, closed balloons were placed in each flute. After impregnation and partial drying the panel was placed in a vacuum chamber (5×10^{-5} torr) and drying was completed. The residual air in the balloons expanded under vacuum and opened the flutes. The surface of the panel had a corduroy appearance due to bulging of the flutes between the transverse webs.

A flat 4-ply glass cloth laminate (8 x 8 inches) was prepared with a mold-release agent (silicone) spread over the surface of the middle two plies to prevent adhesion. The laminate was prepared by pressing the prepregs along the outer 1 inch only. When this laminate was conditioned overnight in a 100% humid atmosphere and then placed in a vacuum chamber (0.1 mm Hg) the laminate inflated to a flat pillow and rigidized in this form.

A 10 inch diameter cylinder, 15 inches long was fabricated from gelatin-impregnated Raypan. This was done by shaping the Raypan around rings to form a cylinder using mandrels in every other flute to provide longitudinal support. The mandrels also served the purpose of keeping the flutes open. This assembly was impregnated with urea (20%) plasticized gelatin. Several dippings were made to obtain a heavy coat of gelatin, thereby sealing the Raypan to make it airtight. The mandrels were removed after successfully coating alternate flutes.

After the assembly had dried, the open ends of the Raypan cylinder were closed with circular wooden discs. The ends were sealed using wet gelatin-impregnated glass cloth. The cylinder was then dipped in gelatin to close any remaining holes. The cylinder was conditioned over water to make it flexible, and collapsed by pumping a vacuum on the inside of the structure. The collapsed cylinder was placed in a vacuum chamber. Inflation was rapid and the structure inflated to a smooth well-formed cylinder. Rigidization occurred as the sample lost water. On sectioning the structure at the end of the test, the flutes were found to be open.

5. Chemical Modification of Gelatin

a. Work discussion

Work was performed on the chemical modifications of gelatin, directed toward producing an internally (chemically reacted) plasticized gelatin which could subsequently be cross-linked by the addition of a catalyst. The particular approach to the problem was to react gelatin with small molecules containing unsaturated bonds to break up internal hydrogen bonding of the gelatin molecule and to produce plasticization. A water soluble, unsaturated compound was used along with the modified gelatin to produce further plasticization and to give a means of cross-linking the modified gelatin in the presence of a catalyst. Maleic anhyrdide and allyl glycidyl ether were investigated as reactive compounds to combine with the reactive sites of the gelatin to produce amides, esters, and modified amines containing ethylenic or allylic functions. It was found that these reactions appeared to proceed quite readily. These modified gelatins were dissolved in aqueous solutions of acrylic acid and acrylamide. A redox catalyst system was subsequently added to effect polymerization of the unsaturated compounds present. Initial work demonstrated that:

(1) Gelatin plus acrylamide gave a clear solution which dried to an opaque white film which was quite flexible but weak (1000 psi tensile strength).

(2) Gelatin plus acrylamide plus a redox catalyst gave an immediate exotherm and a translucent film.

(3) Gelatin plus allyl glycidyl ether (acid catalyzed) gave a translucent solution which became clear on adding acrylamide solution. An immediate exotherm resulted on adding a redox catalyst. The film was clear and softened in hot water (80-100°C) but did not dissolve.

(4) Gelatin was reacted with maleic anhydride under slightly alkaline conditions (pH 8.0 - 9.5) with the following results:

   (a) Films cast from maleic modified gelatin resulted in clear, strong films on drying, with isolated milky areas scattered through the film.

   (b) Maleic-modified gelatin plus acrylic acid solution plus a redox catalyst gave no noticeable exotherm, and produced a sticky film which had a crystalline appearance.

   (c) Maleic-modified gelatin plus acrylamide solution and a redox catalyst gave a solution which produced a clear film on drying. When the above system was cast on Mylar, the modified gelatin solution did not appear to wet the Mylar as unmodified gelatin does. The dry film was brittle and broke easily during removal from the Mylar.

Gelatin was reacted with allyl glycidyl ether (AGE) in aqueous solution at four different pH values (3.0, 4.5, 6.5 and 9.0). U. S. Patent 2,900,267 reports the reaction of styrene oxide and ethylene or propylene oxide with animal glue and aqueous systems at pH 6.5. The solutions resulting from these reactions were opalescent and yellow in color. Clear films could be prepared from them.

Flexible films, which remained flexible, could be produced by adding Acrylamide monomer solutions to AGE-modified gelatin solution. They had the "feel" of a plasticized vinyl polymer.

The AGE-modified gelatin-acrylamide solution, when treated with a redox catalyst to effect cross-linking, showed a marked dependence on the pH of the reacting mixture as shown below:

pH	Comment
3.0	Insolubilization and gelation delayed. Clear films could be cast.
4.5	Gelation within 15 seconds after adding catalyst.
6.5	Gelation immediately.
9.0	Gelation slightly delayed.

It appeared that working at low pH values resulted in workable systems that could be cast into films. At higher pH values, gelation was too rapid to give usable films. The material resulting from rapid gelation (pH 4.5) was definitely insoluble but swelled and became weak when exposed for two hours to hot water (93-100°C). Films prepared from AGE-gelatin solutions (pH 3.0) and acrylamide dried to rigid materials.

Further emphasis was placed on the reaction of allyl glycidyl ether with gelatin to give a modified gelatin containing reactive sites (olefin linkages) capable of reacting with unsaturated water soluble monomers (acrylamide and acrylic acid) to give cross-linked products. The results can be summarized as follows:

(1) Films of AGE modified gelatin have lower tensile strengths than unmodified gelatin (8500 vs 13,000 psi) and slightly increased elongations (6-18% vs 6-8%).

(2) A film of AGE modified gelatin plus acrylamide (50% based on AGE-gelatin) a monomeric unsaturated plasticizer, had low strength (300 psi) and high elongation (270%).

(3) AGE modified gelatin (50%) and acrylamide monomer (50%) produced cross-linked films when cured with a redox catalyst and had a tensile strength of 10,500 (80% of unmodified gelatin) and an elongation of 5.6%.

(4) The strenth of AGE modified gelatin and acrylamide films is influenced by the amount of catalyst used to effect cross-linking (Nos. 9 and 10, Table 13).

(5) Curing of AGE modified gelatin films along with redox catalysts gave inconsistent results. In one case relatively high strengths (8000 psi) and low elongation were obtained. In two cases, strengths were low (2300-2400 psi) and elongation high (100%). This was probably due to undercuring of the material.

It was shown that allyl glycidyl ether modified gelatin-acrylamide film (25% acrylamide based on weight of film) could be insolubilized by passing a mixture of sulfur dioxide (7 volume percent) and air through the film.

The film was mounted in a diffusion cell, with 1 mm Hg pressure on one side of the film, and a slightly greater than atmospheric pressure (815 mm Hg) of the mixed gas imposed on the other side of the film. After several hours diffusion of the mixed gas through the film, the film was found to be insoluble in boiling water. It did swell and become fragile under the influence of hot water. The small sample size precluded determining any mechanical properties of the cured film. On a qualitative basis (appearance and handling), the film was frosted in appearance, strong, and brittle.

TABLE 13

PROPERTIES OF MODIFIED GELATINS

Sample No.	Gelatin Modified With	pH of Solution	Tensile Strength psi	Elongation %
1	Allyl glycidyl ether	6.5	8,600	18.0
2	Allyl glycidyl ether	6.5	8,700	5.9
3	Allyl glycidyl ether	4.5	8,100	18.2
4	Allyl glycidyl ether	3.0	9,532	12.5
5	Allyl glycidyl ether plus redox catalyst system	6.5	8,000	5.9
6	Allyl glycidyl ether plus redox catalyst system	6.5	2,200	115.7
7	Allyl glycidyl ether plus redox catalyst system	6.5	2,400	100.4
8	Allyl glycidyl ether plus acrylamide monomer	4.5	360	270.4
9	Allyl glycidyl ether plus acrylamide plus redox catalyst system	3.0	10,500	5.6
10	Allyl glycidyl ether plus acrylamide plus increased amount of redox catalyst system	3.0	7,500	4.6

APPENDIX C

GELATIN CHEMICAL MODIFICATION

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A. OBJECTIVE

The principle objective of this effort was to modify gelatin to provide an optimum rigidizing material for both space and terrestrial application which could be vapor catalyzed.

B. CONCLUSIONS

1. All attempts to chemically modify gelatin resulted in a weakening of physical strengths. This is evident from the data recorded in Table 14.

2. Rigidization of chemically modified gelatin glass laminates by vacuum desiccation exhibited considerably lower flexural strengths than laminates that were pressure-heat cured (Table 15).

3. A graft copolymer of ethyleneimine and gelatin, cross-linked with a reactive difunctional compound such as butadiene diepoxide, produced an insoluble gel which resisted water reabsorption. Data from Table 16 show that the higher the percentage of cross-linker used the lower the percent of water absorbed by the gelatin.

4. Chemical modification of gelatin increased the thermal stability of the polymer.

C. DISCUSSION OF RESULTS

The amino acid composition of gelatin consists primarily of residues containing proline, hydroxyproline, and glycine. With the statistical distribution of the amino residues present in the molecule, a carboxyl or basic group (amino or guanidino) occurs on every twenty-fifth or thirty-third backbone atom respectively. With cross-linking available at these chemically active sites, the approach taken was to employ polymeric materials. Thus, the large regions of the gelatin molecule left between cross-links would be spatially entwined with the backbone of the polymeric additive. This type of modification would serve two purposes:

TABLE 14

FILM AND LAMINATE STRENGTHS OF MODIFIED GELATIN

Sample Composition		H_2O Solubility	Free Film Strength		Laminate 181 Glass 3 ply	
Swift Gelatin Acid Processed	% Modifier		Tensile psi	% Elongation	Flexural Strength psi	Flexural Modulus psi
	Control	Sol	11,500			
	5% Genamide	Sol	1,300	5.0		
	15% Genamide	Sol	5,050		12,000	2.0×10^6
	25% Genamide	Sol	5,000			
	25% SMA 4000	Sol	4,600	2.0	10,000	1.1×10^6
	25% 	Sol	5,000	4.6	43,000	3.6×10^6
	F* + 	Insol			47,500	3.2×10^6
	F* + 20% Epirez 500	Insol			23,000	1.9×10^6
	5% Octadecyl isocyanate + 10% Butyrolactone	Sol	10,366	3.0		
	3% Dicyclohexyl Carbodiimide	Insol	9,000		27,500	2.6×10^6
	12% Dicyclohexyl Carbodiimide	Insol	2,116	4.8	15,560	2.0×10^6
	25% Dicyclohexyl Carbodiimide	Insol	Too brittle			
	10% Butadiene diepoxide	Insol	4,700	2.0	23,560	2.7×10^6

F* - represents graft copolymer of gelatin and ethyleneimine.

TABLE 14 (CONT'D)

FILM AND LAMINATE STRENGTHS OF MODIFIED GELATINS

Sample Composition		H_2O Solubility	Free Film Strength		Laminate 181 Glass 3 ply	
Swift Gelatin Acid Processed	% Modifier		Tensile psi	% Elongation	Flexural Strength psi	Flexural Modulus psi
Thiolated Gelatin	50% 	Sol	4,076	4.0		
		Insol			16,000	2.8×10^6
Thiolated Gelatin	10% Glyoxal	Insol	8,000	3.0	21,000	2.1×10^6
	10% Vinylene isocyanate	Insol	6,500	2.6	17.00	2.3×10^6
	5% Cu Phthalocyanine dissolved in 70% genamide 250		1,450	2.0		
Control		Sol	11,800	5.0	46,000	3.6×10^6

TABLE 15

COMPARATIVE LAMINATE STRENGTH

Sample	Heat Pressure[1] Flexural Strength psi	Laminate[2] Flexural Modulus psi	Vacuum[3] Dessicated Flexural Strength psi	Laminate Flexural Modulus psi	% Resin
1. Gelatin-ethyleneimine graft copolymer	43,000	3.6×10^6	16,000	1.9×10^6	45
2. Gelatin-glyoxal	21,000	2.1×10^6	13,500	1.7×10^6	43
3. Gelatin-vinylene diisocyanate	17,000	2.3×10^6	10,000	1.3×10^6	40
4. Gelatin	46,000	3.6×10^6	18,000	2.1×10^6	42

1. A pressing temperature of 130°C and 1000 psi for 10 minutes was used.
2. All laminate specimens consisted of 3 ply 181 glass Volan treated.
3. Vacuum conditions were 5×10^{-5} mm Hg for 24 hours.

TABLE 16

WATER ABSORPTION OF MODIFIED GELATIN

Sample	Cross-Linker	H_2O Absorptivity % Weight[1]
1. Gelatin-ethyleneimine copolymer	8% Butadiene diepoxide	180
	15% Butadiene diepoxide	66
	66% Butadiene diepoxide	33
	88% Butadiene diepoxide	10
	20% Epirez 500	33
	40% Epirez 500	24
	10% $CrCl_3$	480
2. Gelatin	10% Cyclohexyl Carbodiimide	66
3. Gelatin	10% Glyoxal	120
4. Gelatin	10% Vinylene diisocyanate	145

1. Gelatin insolubilized samples immersed in boiling water for one hour.

1. Chemically modify gelatin to leave residues capable of cross-linking via gas catalysis, and

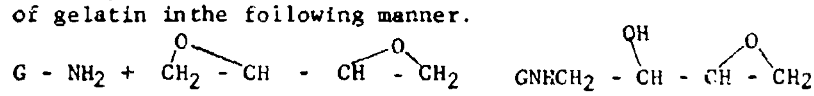
2. Reduce the tendency of the gelatin macromolecule to reabsorb water.

Two types of polymeric materials were evaluated: styrene-maleic anhydride (acidic residue), and Genamide 250, a fatty acid amino amide (basic residue). Both were reacted in varying proportions from 5 to 30 percent with a 40 percent gelatin-water-ethylene chlorohydrin solution. The products obtained formed water soluble gels from which clear films were cast. In each case, the physical properties of the films were poor as shown in Table 14. Monomeric additives will be discussed individually. Physical properties are described in Table 14.

D. EXPERIMENTAL

1. Butadiene Diepoxide

The reaction of the diepoxide with anhydrous gelatin was carried out in an anhydrous solvent (generally benzene or dioxane) as a suspension phase at 40°C with efficient stirring. After removal of the solvent, the dried residue was readily soluble in water. This type of reagent reacts probably through the amino and hydroxyl residues of gelatin in the following manner.



Butadiene diepoxide was used at several concentrations: 2, 5, 10 and 50 percent based on total gelatin solids. It was hoped that the residual oxirane would be available for reaction and additional cross-linking with a gaseous catalyst; however, it is very likely that it underwent ring opening in the majority of instances. It was impossible to detect oxirane chemically or through spectroscopic analysis. This chemical modification resulted in a loss of strength and increased water solubility. The thermal stability of the modified gelatin improved as was interpreted from Differential Analysis Thermograms.

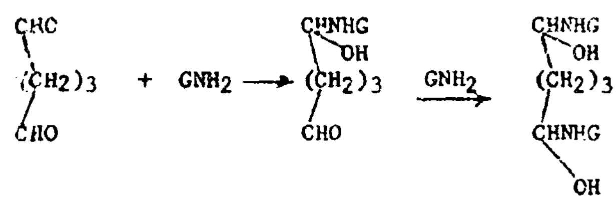
2. Glyoxal

The reaction of this dialdehyde with gelatin was performed in an aqueous media. Gelation was rapid in this instance. Desiccation of the residue yielded a hard, horny solid which was insoluble in boiling water, but reabsorbed water as evidenced by the increase in volume and weight. This type of reagent reacts through the amino residues of gelatin in the following manner.

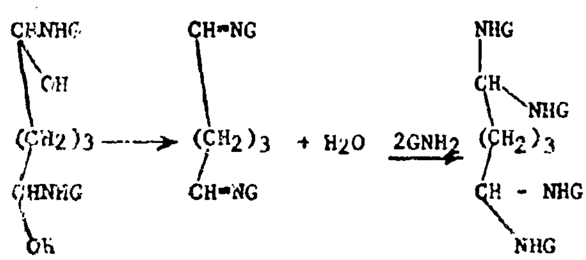
Glyoxal was used at several concentrations, 2, 5, 10, and 20 percent based on total gelatin solids. Free films could not be cast due to the insolubility of the cross-linked material. Physical strengths of glass laminates were low. Thermal stability of the modified gelatin was not improved.

3. Glutaraldehyde

The reaction of glutaraldehyde with gelatin was much faster than glyoxal and produced a water insoluble gel. A possible reason is that glutaraldehyde may form a longer link than glyoxal with a resulting greater probability of completing the cross-link with the second aldehyde as shown below

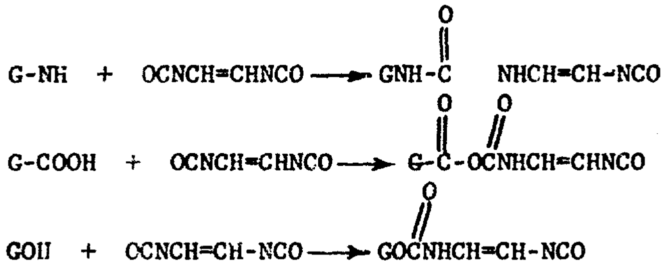


Another possibility is that if the glutaraldehyde half link can react with another amino group via a Schiff base, then glutaraldehyde might be a tetra-functional cross-linking agent as shown.



4. Vinylene Diisocyanate

The diisocyanate was reacted with anhydrous gelatin in anhydrous solvents. Vinylene diisocyanate was used in 1, 5, 10 and 30 percent, based on total gelatin solids. This type of reagent reacts through the carboxyl, amino, hydroxyl and guanidino (all being active hydrogen containing materials).



Residual functionality remaining in the gelatin residue would be capable of further cross-linking via gaseous catalysis; however, this chemical modification resulted in insoluble gel formation. In this instance, the physical strength was poor, although the thermal stability increased (Table 14). Infra-red spectrographic analysis indicated trace absorption at 2250 cm^{-1} for free NCO. The chemical modification of gelatin by reaction with such an organic isocyanate has been improved by conducting the reaction in the presence of butyrolactone which facilitates and promotes the reaction. The effective action of butyrolactone as a catalyst for the reaction of isocyanates with gelatin was exemplified by the following comparative tests:

a. Anhydrous gelatin (1.2g) and the isocyanate (.5g) were heated in dry dioxane for 30 minutes. The gelatin was washed with acetone and ethanol to remove the unreacted reagents and dried. It was found that the increase in weight of the gelatin was only 4 percent.

b. Dry gelatin (1.2g), and γ-butyrolactone (5 ml), were heated at 120°C for two hours. The gelatin was washed as described above and dried. The increase in weight of the gelatin was only 2 percent.

c. Dry gelatin (1.2g) was heated with the isocyanate (.3g), and γ-butyrolactone (4 ml), at 120°C for 30 minutes. The gelatin was washed as described above and dried. In this case, the increase in weight of the gelatin, due to the reaction with the isocyanate, was 37 percent.

Other diisocyantes were evaluated and behaved similarly. These included commercial toluene diisocyanate, hexamethylene diisocyanate, and m-phenylene diisocyanate. Water insoluble modifications were formed in each instance, however, the modified gelatin showed no improvement in physical properties.

5. Octadecyl Isocyanate

This monomeric isocyanate was reacted in the same manner as the diisocyanates described above. The differentiating feature of this modification was its water solubility. This enabled free films to be cast which were nearly as strong as those obtained from unmodified gelatin.

6. Dicyclohexyl Carbodiimide

The use of carbodiimides as hardeners for gelatin has been known for some time. To evaluate this cross-linking reagent, it was necessary to run the reaction sequence in an anhydrous media. The solvent system chosen for this reaction was Carbowax 600, a commercial polyether. Dicyclohexyl carbodiimide in varying proportions of 3, 12, and 33 percent by weight were added to the gelatin-Carbowax suspension and heated to 60°C for one-half hour. Upon adding water to the reaction, a hard dry gel formed which became harder on storage under room conditions. Although physical strengths were weaker than observed with unmodified gelatins, they were higher than generally observed from other chemically modified gelatins. In addition, this modification absorbed water to a lesser extent than generally observed with others. The net reaction is probably as given below:

$$R\text{-}N{=}C{=}NR \;+\; GNH_2 \;+\; GCOOH \qquad G\overset{O}{\overset{\|}{C}}\;\overset{H}{\overset{|}{N}}\text{-}G \;+\; R\overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}}\;\overset{H}{\overset{|}{N}}R$$

where R = an aromatic radical.

7. Formaldehyde

An acceleration of formaldehyde cross-linking of 20 percent gelatin at 35°C was observed when low concentrations of urea were added to the gelatin before the addition of formaldehyde. This may be explained by assuming that urea is also reacting with gelatin to afford more accessible amino groups. At a higher urea concentration, the effect is obscured by the reaction of urea and formaldehyde. Interestingly enough, this acceleration was not observed at 45°C in more concentrated solution. This suggests that the acceleration involves gelatin hydrogen bonds and urea at 35°C, since little hydrogen bonding would be expected at 45°C. This work with formaldehyde cross-linking was reported by I. M. Robinson and verified by investigation. Sample structures were impregnated with plasticized gelatin solutions containing trace amounts of urea and gassed with formaldehyde. Gelation occurred but rigidity was not achieved due to the plasticizing action of Carbowax 600 used as a co-solvent which was necessary to prevent rigidization via solvent boiloff.

8. Ethylene Imine

In another attempt at modification, gelatin was digested for one week in a 10 percent aqueous ethylene imine solution. A water soluble gel formed. After removal of any trace unreacted monomer, clear 20 mil films were cast and dried. The physical strengths of the films were inferior to those obtained from unmodified gelatin. Complete desiccation of a portion of the gelled product left a gelatin-ethylene imine copolymer that exhibited greater thermal stability than obtained from unmodified gelatin. (Table 14) The most probable reaction is illustrated in the following reaction.

$$GNH_2 + HN \longrightarrow -[GNHCH_2CH_2NH]_x - NH_2$$

The water soluble graft copolymer when reacted with butadiene diepoxide gelled instantaneously into a completely water insoluble material even at boiling temperatures. The higher the percent of butadiene diepoxide used to cross-link the copolymer, the greater the water insensitivity of the cross-linked copolymer. An 88 percent concentration of butadiene diepoxide yielded a copolymer which absorbed only 10 percent water by weight after immersion in boiling water for one hour. (Table 16). A heat pressure cured gelatin-ethylene imine copolymer and 3-ply 181 glass laminate, had an average flexural strength of 43,000 psi and a flexural modulus of 3,600,000 psi. Conditioning a similar laminate by soaking in butadiene diepoxide for a number of hours prior to heat-pressure curing, gave a laminate exhibiting higher flexural strength (47,500 psi) and a lower flexural modulus (3,200,000 psi).

Polymeric epoxy resins reacted with gelatin-ethylene imine graft copolymer were observed to have slower gelation rates. Since graft gelatin-butadiene diepoxide cross-linked copolymer laminates could not be directly prepared by dip saturation due to instantaneous gelation, it was hoped the slower gelling polymeric epoxy reaction products could be more easily impregnated and laminated.

The addition of 25 percent by weight itaconic anhydride to the gelatin-ethylene imine copolymer produced a water soluble solution. A trace of free radical precursor was added and a clear film cast on a glass panel. An orange film developed upon heating which was too hard and brittle to remove.

9. Phthalocyanine and Metal-Phthalocyanine Complexes

Copper phthalocyanine was synthesized for evaluation as a potential gelatin modifier. The copper phthalocyanine was solubilized in Genamide 250 containing 20 percent ethylene diamine. To this solution was added an aqueous ethylene chlorohydrin solution of 40 percent gelatin. A gel formed which was insoluble in boiling water although it swelled considerably. The free carboxyl groups of the phthalocyanine react with primary amines to form a soluble salt complex. The free remaining amino groups of the polyamine would then react as usual with the acidic functionality of the gelatin molecule to yield a very bulky, rigid, unorientated, modified material. It was hoped this could give substantial water re-absorption resistance; however, this was not realized. Physical strengths of the system were drastically reduced.

10. Thiolated Gelatin

Reaction of gelatin with specific thiolactones yielded free sulfahydrl groups. Once these were converted to stable disulfide bonds, the disulfide cross-linked gelatin modification was insoluble in boiling water; however, as is generally found, it swelled considerably in water. These cross-linked gels can be redissolved in water by the addition of an appropriate reagent such as molar solutions of potassium thiocyanate or lithium chloride. Physical strengths of this product and other attempts to modify the thiolated gelatin gave no improved strength characteristics.

APPENDIX D

THE STUDY OF COLLAGEN AND ITS DERIVATIVES FOR USE IN SPACE AND TERRESTRIAL STRUCTURES

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A. OBJECTIVES

The objectives for this study were to evaluate collagen and its derivatives as a potential raw material for structures suitable for use in space, and, if possible, terrestrial environments. This was to include the preparation of collagen in its naturally woven state, reconstituted and oriented commercial collagen films, and collagen films cast from collagen solutions as prepared in the laboratories.

Films were to be evaluated in their native state as well as after cross-linking with various tanning agents. The best of these, as determined by strength tests, were to be used to make small scale structures to produce visual specimens for examination.

B. CONCLUSIONS

1. Collagen films do not possess strengths superior to gelatin except in those instances where fortuitous film orientation is achieved.

2. Saturated native or tanned corium collagen films did not produce t e expected tensile strengths and gave extremely brittle films.

3. Collagen films adhered to gelatin and made into multiple ply laminates did not produce stronger structures.

4. Commercial collagen cords soaked and saturated in warm gelatin solutions prior to twisting and stretching until dry produced the best overall results.

C. EXPERIMENTAL

This section describes the work performed with native collagen obtained from hides, processed in various ways, and collagen films from commercially available sausage casings. Native collagen films prepared from hides lacked uniformity primarily because of the unavailability of high pressure filter screens for removing uncured particles and hair fibers. Comparisons of strengths of cross-linked films with plain films were inconclusive. Therefore, it was decided to evaluate the characteristics of commercially processed collagen in the form of sausage casings, which are more uniform and free of foreign material.

The work described does not necessarily follow the exact order in which it was done, but is divided into sections dealing with native collagen and commercial collagen.

1. Preparation of Native Collagen from Hides

Native collagen was obtained from the hide of a steer. The hide was soaked in ammonium hydroxide to remove the hair and split by machine into layers about 1 mm thick. The layers were cut into small pieces and degreased by solvent extraction. Since the corium layer of the hide represents the strongest layer of collagen fibers, that layer was selected as a collagen source. The corium was pulverized by passing it with ice through a Urshel mill with a 0.02 inch pestle. The material was then screened under pressure to remove extraneous matter after dilution to about 2% solids.

The second phase in preparing the collagen was the acid or alkali cure to produce the hydrated collagen gel for final shaping, extrusion or casting.

a. Films Prepared from Acid-Cured Collagen

Films were prepared from the corium collagen, cured with four different acids, namely: hydrochloric, acetic, sulfamic, and lactic acids. The collagen was softened with water and the particular acid at about 1-½% concentration of protein in the aqueous acid. Curing proceeded at 4-7°C followed by pressure screening and deaerating under vacuum.

The resulting heavy gel was spread on Mylar-coated glass plates at a wet thickness of ½-inch and air dried 48 hours. The film was then neutralized with ammonia, dialyzed to remove soluble salts, defatted, and finally air dried for testing.

Of the four acids, sulfamic and lactic resulted in the strongest non-oriented films. Therefore, an attempt was made to optimize the curing conditions for collagen employing these two acids over a narrow range of pH. Results obtained from these two acid tests are shown below.

ACID TESTS OF COLLAGEN FILMS

Lactic Acid

pH of Curing System Using Lactic Acid	Tensile Strength of Degreased Films	Tensile Strength of Films Not Degreased
3.25	13,500	-
3.05	11,200	10,200
2.85	13,700	-
2.70	9,800	11,400
2.55	-	13,000
2.45	-	12,000
2.35	10,000	10,400

Sulfamic Acid

pH of Curing System Using Sulfamic Acid	Tensile Strength of Degreased Films	Tensile Strength of Films Not Degreased
3.10	-	10,000
2.75	14,000	-
2.50	-	10,500
2.30	-	10,900
2.15	12,400	-

The data showed that the acid concentration was not critical as long as the pH was low enough to effect complete hydration of the collagen without degradation. It may further be concluded that degreasing was not critical unless fat contents rose above a certain minimum.

It was evident that slight changes in humidity exerted a more pronounced effect on the ultimate strength of the fiber than did many of the other variables. This will be further demonstrated in a later section in this report where commercial cords are discussed.

(1) Collagen-Gelatin Films

Attempts were made to improve the strength properties of collagen by blending it with gelatin. The collagen was prepared using the lactic acid method of cure at a pH of 3. This particular pH was chosen to avoid excess acidity which might have produced hydrolysis of the collagen as it was blended in the warm gelatin solution. It was found that dispersing the collagen into a fairly low gelatin concentration (2-½%) in water resulted in better deaeration in a vacuum than when using higher concentrations.

Blending was accomplished in a Hobart Dough Mixer and when uniform the material was filtered and deaerated in a vacuum. The samples were prepared using collagen-gelatin ratios of 1:1, 1:2, and 2:1. They were dried and tested for tensile strengths. The results of this experiment are shown below:

Collagen-Gelatin Ratio	Tensile Strengths Ammonia Neutralized	Tensile Strengths Not Neutralized
1:2	10,500	11,700
1:1		10,000
2:1		12,400

b. Films Produced with Alkali-Cured Collagen

Alkaline-curing agents were also investigated, namely; saturated lime water, diethanolamine, ammonium hydroxide and sodium hydroxide. The first three of these alkaline materials failed to produce the degree of swelling required to promote sufficient hydration for the casting of films. Lime itself would have to be used over a curing period of 4 weeks to promote adequate swelling. These milder alkalies were not pursued further.

Sodium hydroxide was used at two levels, namely: 4% and 8% basis hide corium stock. The curing procedure was essentially the same as when acids were employed. The data show that lower strengths resulted when collagen was alkali cured than those resulting from acid cures.

Curing Solution	% Alkali Basis Collagen	pH of Cure	Tensile Strength
NaOH	4	12.9	9600 psi
NaOH	8	13.2	10300 psi

c. Collagen Films from Vegetable-Tanned Leather

When the corium was processed for fat and moisture removal, a flexible, porous fibrous sheet resulted. It was hoped that such a material would provide an excellent matrix for saturation with gelatin solutions, but it became apparent saturation was, in fact, difficult if not impossible to effect. It was decided to perform further saturation work on vegetable-tanned leather.

Samples were obtained from the A. C. Lawrence Leather Company in the wet state. They were air dried and defatted prior to use. Attempts to impregnate the splits by soaking them in a 35% gelatin/water solution were not successful. It was felt that air in the vegetable-tanned splits prevented the impregnation of gelatin.

An attempt was made to displace the air with 25, 50, and 75% N-methyl pyrolidone and methyl butynol solutions in water by soaking the samples in the various solutions for 24 hours. Impregnation was then again attempted in the 35% gelatin solutions at 130°F for from 1 to 2 hours.

The samples were then removed, drained of excess gelatin, dried, pressed and tested for tensile strength and modulus. The following list summarizes this test data.

DEAERATING SOLVENT	IMPREG-NATING SOLUTION	TEMP OF IMPREG-NATION	TENSILE STRENGTH PSI	YOUNG'S MODULUS PSI
25% N-Methyl pyrrolidone in water	35% Gelatin in Water	125°F	5470	4.7×10^5
50% N-Methyl pyrrolidone in water	"	"	4480	2.1×10^5
75% N-Methyl pyrrolidone in water	"	"	4070	1.5×10^5
25% Methyl butynol in water	"	"	6330	4.3×10^5
50% Methyl butynol in water	"	"	7330	4.0×10^5
75% Methyl butynol in water	"	"	5830	4.4×10^5

In each instance the impregnated leather split was weaker than the gelatin alone as determined for unsupported films. Yet, the saturation was considered to be complete because the impregnated split was very translucent.

The stiffness was markedly enhanced since all the normal flexibility of the leather split was removed by the impregnation. Of particular interest, was the stiffening effect of N-methyl pyrrolidone when used as a deaerating solvent in a 25% aqueous solution. More concentrated solutions of the N-methyl pyrrolidone appeared to plasticize, probably because of the hygroscopicity of the solvent and its low volatility. Methyl butynol, being much more volatile, yielded somewhat higher tensile strength and stiffness. In every instance, however, the saturated vegetable-tanned leather splits were weaker than the unsupported gelatin film alone.

Another approach to the problem of impregnating the splits was the use of a more dilute solution of gelatin for the purpose of saturating the splits and driving out the air. Those deaerated splits were then further impregnated using higher levels of gelatin concentrations. Incomplete saturation resulted and was confirmed by the increased flexibility of the material. Uncoated fibers were noted in the middle of the sample when it was bent double.

Untanned corium samples were also soaked in warm gelatin solutions. The samples were dipped in 10 and 15% gelatin for 30 minutes until they became translucent and then transferred to warm 35% solutions and worked mechanically. After drying, the sheets were conditioned at 80% RH and tested. Tensile strengths averaged only 6800 psi. Again, it was apparent that there was no enhancement of strength by the gelatin.

2. Preparation of Collagen Films from Commercial Products

In order to investigate the properties of highly refined and oriented collagen, two grades of commercial sausage casings normally used in food products were obtained. These were of two types: a 2 mil casing produced by Brechteen, and a ½-mil casing produced by Devro Corporation.

The casings were prepared for various treatments by washing with a detergent and defatted by solvent extraction. The Brechteen had been tanned with smoke and formaldehyde and the Devro with aluminum salts.

a. Hydrating Commercial Collagen

Since these collagen films had a tensile strength in the 11-13,000 psi range, it was thought that a more continuous film with higher strengths could be prepared by treatment with various hydrating solvents. The solvents studied were 25% and 80% aqueous solutions of N-methyl pyrrolidone, dimethyl sulfoxide, dimethyl-formamide, and methyl butynol. Films treated in this manner were compared with the commercial Brechteen as received, after washing, and washing after degreasing.

This data is in the following list:

TREATMENT	TENSILE STRENGTH
Brechteen film as received	13300 psi
Brechteen film washed (24 hrs)	14700
Brechteen film washed and degreased	16900
25% aqueous N-methyl pyrrolidone	13900
80% aqueous N-methyl pyrrolidone	14400
25% aqueous N-methyl pyrrolidone	13300
80% aqueous N-methyl pyrrolidone	13000
25% aqueous dimethyl-formamide	14200
80% aqueous dimethyl-formamide	14600
25% aqueous methyl butynol	14900
80% aqueous methyl butynol	13500

Vigorous treatment with formaldehyde was effected in order to determine whether any greater strength could be expected. Washed, degreased Brechteen collagen was treated at various pH with different concentrations of formaldehyde for 24 hours. Dried films were tested for tensile strength at room temperature before and after 1 hour of heating at 60°C.

Formaldehyde Concentration	pH	Room Temp. 25°C	1 Hour Heating At 60°C
0.2%	6.7	13300	13800
1.0%	6.4	13400	13200
1.0%	8.2	11500	12400
5.0%	5.6	12700	12600

The data show that some enhancement of strength could be achieved by treatment with formaldehyde, but this was decreased with increasing severity of the reaction conditions.

b. Detanning with Urea

The Brechteen and Devro films were soaked at room temperature in 20% urea solution to regenerate the native collagen if possible. The reagent was removed by washing in cold water and the film was redried under tension.

c. Reaction with Formaldehyde

The heavier Brechteen collagen film was soaked in 1% formaldehyde solution for 15 minutes and for 1 hour. Specimens were rinsed and dried under tension as before.

d. Reaction with Hydrogen Cyanamide

The Brechteen collagen was soaked in 2% aqueous cyanmide solution and after washing, was dried under tension as before.

e. Reaction with Epichlorohydrin

As in the above reaction, Brechteen collagen was treated with a 5% solution of epichlorohydrin in 25% aqueous ethanol and after 15 and 60 minute periods were washed and dried as before.

Standard specimens were stamped out using a die and Carver press against an aluminum plate. Measurements were made on the Instron machine using 0.05 inches/minute as the rate of jaw separation. The following list shows these results:

Film	Treatment	Tensile Strength lbs/in^2
Brechteen	Washed and degreased	16.9×10^3
Brechteen	Urea detanning	13.2×10^3
Brechteen	Formaldehyde 15 min.	14.7×10^3
Brechteen	Formaldehyde 60 min	16.8×10^3
Brechteen	Hydrogen cyanamide 15 min	14.8×10^3
Brechteen	Hydrogen cyanamide 60 min	15.3×10^3
Brechteen	Epichlorohydrin 15 min	13.4×10^3
Brechteen	Epichlorohydrin 60 min	13.3×10^3
Devro	Washed and degreased	13.6×10^3
Devro	Urea detanning	10.9×10^3

Based on these studies, the following conclusions were drawn.

(1) Formaldehyde or some other aldehyde cross-linkage will produce maximum strengths since reversal by means of an aldehyde scavenger (urea) lowered the tensile strength but it could be restored by recombining with formaldehyde.

(2) The Devro collagen was alum tanned and gave weaker results which was not unexpected.

f. Saturation of Commercial Collagen with Gelatin

Washed, degreased Brechteen collagen was soaked in water at 60°C and in 35% gelatin/water at 60°C for 15 minutes. After drying, the gelatin/collagen laminate separated simply by flexing, there was no indication of adhesion or penetration.

Another sample was first soaked in 25% methyl butynol/water at 60 C. After soaking this sample in 35% gelatin as before, and drying, the laminate was bent and snapped clearly with no sign of delamination. However, when this sample was immersed in cold water, the gelatin layers softened and peeled off. It can be assumed that the methyl butynol improved the adhesion of the gelatin and the collagen.

g. Devro Collagen-Gelatin Cords

During this effort, it has not been possible to extrude fibers, films, or tubes of collagen because of the lack of necessary equipment. However, the high strength of cat gut and similar materials warranted further experimentation.

Devro collagen casings were cut into strips and soaked in 15% gelatin solution at 45°C for 15 minutes. As the soft-soaked strips were removed from the gelatin solution they were twisted and stretched by hand and finally suspended under mild tension for drying at ambient room conditions. Tensile strengths were determined on five separate specimens as shown in the following list:

Cord Diameter	Cross-Sectional Area	Tensile Strength
.0391 in.	1.20×10^{-3} sq. in.	23,300 psi
.0391 in.	1.20×10^{-3} sq. in.	22,600 psi
.0468 in.	1.72×10^{-3} sq. in.	11,200 psi
.0468 in.	1.72×10^{-3} sq. in.	14,200 psi
.0468 in.	1.72×10^{-3} sq. in.	13,200 psi

Although it was impossible to accurately determine the cross-sectional area at the point of breakage, it was felt that the measured dimensions were larger than the actual dimensions. This was not a sufficient number of samples for firm conclusions. It appears, however, that collagen fibers may be very attractive for expandable structure application. Modulus of elasticity values were not determined.

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In the search for optimum materials for use in an expandable sandwich concept of fabricating space structures, a gelatin rigidizing resin system was improved and adapted for use to rigidize space structures. It was demonstrated that a protein system is a desirable system for use with fabric materials. The system provided an easily applied, high strength, space environment resistant material which offers good promise for use in actual space systems.

The final items of the development program were lightweight, self-rigidizing 2-1/2 ft diameter solar energy concentrators and 3-1/2 ft diameter by 4-ft high cylindrical space shelter models. These structures were vacuum cured by a plasticizer boil-off process of a gelatin resin system.

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